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Gasoline Alley, Fort Drum Bioremediation Evaluation, Area 1595, Phase I and Phase II

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Preface

The Study herein was conducted as a part of a site remediation of total petroleum hydrocarbon at Area 1595 located along Gasoline Alley at an active military installation of Fort Drum, New York. This report was prepared at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, in cooperation with the Fort Drum Military Installation, New York, New York State Department of Environmental Control, and the U.S. Army Engineer District, Baltimore. Program Manager for Fort Drum was Ms. Ann Wood. Program Manager for the Baltimore District was Ms. Shelley Spayde. Project Managers were Mr. Jeffrey Talley, Environmental Laboratory (EL), ERDC, and Dr. Rakesh Bajpai, University of Missouri, Columbia. Principal Investigators were Messrs. Lance Hansen and Roy Wade, EL, ERDC.

The bench-scale studies were conducted between March 1997 and October 1997 at ERDC, EL. This report was written by Mr. Scott Waisner, AScI, ERDC contractor; Messrs. Hansen, Talley, and Wade, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Dr. Herbert Fredrickson and David Ringelberg, Ecosystem Processes and Effect Division (EPED), EL, ERDC; and Dr. Bajpai, University of Missouri.

The report was prepared at ERDC under the direct supervision of Mr. Daniel E. Averett, Chief, ERB, and under general supervision of Dr. Richard A. Price, Chief, EED, and Dr. John Keeley, Acting Director, EL.

At the time of publication of the report, Director of ERDC was Dr. James R. Houston, and Commander was COL James S. Weller, EN.

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Executive Summary

The goal of this effort was to evaluate biotreatability options for total petroleum hydrocarbons (TPH) contaminated Area 1595 located along Gasoline Alley at the active duty military installation of Fort Drum, New York. Area 1595 most recently held two 94,600-l (25,000-gal) and one 45,600-l (12,000-gal) underground storage tanks (USTs) used for military refueling and was part of a nine-site refueling complex containing 21 USTs. The objectives of the evaluation were to: (a) determine potential microbial activity of Area 1595 subsurface soils; (b) determine intrinsic TPH degradation potential of Area 1595 subsurface microorganisms; (c) determine parameters which will enhance subsurface microbial growth in Area 1595; (d) optimize parameters using column study simulation of Area 1595 subsurface conditions; and (e) generate data for design and preliminary cost evaluation for the remediation of Area 1595.

Microcosm Studies

Initially, a single 5-m (15-ft) core was taken near well OBG3 from Area 1595 to a depth of 5 m (15 ft). This core traversed the anticipated area of the smear zone. From this core, subsurface contaminant and microbial profiles were developed for Area 1595. Following characterization, soil aliquots from the top and bottom of the smear zone were challenged with radiolabeled acetate in respirometry flask studies to determine the basal microbial activity of Area 1595 subsurface soils. Acetate was chosen for this challenge because it can be easily utilized as a source of energy and/or carbon by most microorganisms. These studies were conducted under unsaturated and saturated conditions to simulate the vadose and saturated zones in the aquifer during seasonal fluctuations. It was determined through the microbial profile and flask studies that the subsurface of Area 1595 contained a healthy and diverse population of microorganisms with a significant metabolic potential, specifically at the top of the smear zone.

Following the acetate challenge, Area 1595 soils were challenged with radiolabeled phenanthrene in respirometry flasks. Phenanthrene was chosen to estimate the intrinsic TPH degradation potentials of the native microorganisms. Phenanthrene is a relatively recalcitrant compound compared with other fuel range hydrocarbons, and as such, phenanthrene degradation results will represent conservative estimates of overall microbial activity on bulk hydrocarbon contamination. The experimental control, exposed only to atmospheric air, resulted in the highest metabolism of the tracer compound. This evaluation indicated that amendments other than molecular oxygen were not necessary to mineralize the recalcitrant contaminant. This suggests that molecular oxygen from atmospheric air is a sufficient amendment to stimulate microbial degradation of hydrocarbon contamination in the subsurface of Area 1595.

Column Studies

Following respirometry flask studies, three additional 5-m (15-ft) subsurface cores were extracted from Area 1595 in July 1997. These cores were extracted within a 3-m (10-ft) radius of the core extracted in March 1997. The final phase of the study consisted of using these cores in packed soil columns operated in parallel. The soil columns were used to compare three alternatives for the remediation of Area 1595: natural attenuation (NA), bioventing (BV), and biosparging (BS). Soil, water, and vapor samples were analyzed over the course of the evaluation. Independent analysis and comparison of each phase were completed and compared among competing alternatives.

Samples were collected from various sampling ports at 2-week intervals following a 7-day equilibration period. Soil samples were taken from ports throughout the column. Water samples were taken from three of the lowest ports of the columns and represented three groundwater zones in the vertical groundwater profile. At each sampling event, all free water was removed from the column and replaced with contaminated groundwater from the site. Off gases from the columns were analyzed daily for concentrations of oxygen and carbon dioxide. These gases were also checked for petroleum hydrocarbons several times during the evaluation. The columns were sacrificed after 10 weeks, and the soil samples were analyzed for recoverable total petroleum hydrocarbons (rTPH) and microbial phospholipid fatty acids.

Initial rTPH and microbial analysis of cores showed a similar vertical contaminant distribution pattern in the cores, but absolute contaminant concentrations differed between cores. rTPH contamination was present predominantly in the soil phase and largely limited to the lower half of the column. Water phase rTPH concentrations increased after the initial 7-day equilibration, confirming that the soil continues to act as a source of contamination. Maximum increases in aqueous-phase rTPH concentrations occurred near the smear zone where soil-phase rTPH concentrations were the highest.

Analyses of soil data suggested that the changes in soil rTPH concentrations over the 10-week evaluation were statistically insignificant for bioventing and natural attenuation conditions. The loss of rTPH in the biosparging column was considerable, and it can be said with 98 percent confidence that an overall reduction of rTPH did occur in the soil column. The zero-order removal rate of rTPH in the biosparging column was $35.5 \text{ mg rTPH kg contaminated soil}^{-1} \text{ day}^{-1}$.

Analyses of pore water data suggested that rTPH present in aqueous phase was being removed from all columns. The first-order removal-rate constants were 0.04, 2.07, and 9.16 day^{-1} for the natural attenuation, bioventing, and biosparging columns, respectively. These removal-rate constants suggest that both biosparging and bioventing will remove rTPH from the aqueous phase, but biosparging will be much more effective for controlling migration of rTPH in the groundwater.

Independent confirmations of rTPH biodegradation in the soils were obtained for bioventing and biosparging columns through the analyses of exit gas data. The exit gas analyses showed production of carbon dioxide and consumption of oxygen in the gas phase (evidence of aerobic metabolism). Respiration coefficients (RQ – ratio of the rate of carbon dioxide production to the rate of oxygen consumption) of 0.78 and 0.68 were observed for bioventing and biosparging, respectively. RQ values in this range suggest metabolization of hydrocarbons. Further more, the respiration activity was sustained throughout the experiment. These data suggested that metabolization of rTPHs in the bioventing and biosparging columns was taking place at a steady rate of 0.33 and 0.49-mg rTPH kg contaminated soil⁻¹ day⁻¹, respectively. These steady-state rates were witnessed with an airflow rate of 1 sccm/min in each column (bioventing and biosparging). This corresponds to specific flow rates of 49-sccm air/kg soil/day in the bioventing column and 50-sccm air/kg soil/day in the biosparging column. The average linear velocity of air in each column was estimated to be 5.6 cm/hr.

1 Introduction

The U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, under scope of work (SOW) agreement with the U.S. Army Corps Engineer District (USAED), Baltimore, conducted a biological treatability study to evaluate three alternative remediation strategies and provide information useful for the design and implementation of long-term remediation activities for Area 1595 of Gasoline Alley, Fort Drum, New York. The project was executed between March and October 1997. To date, one interim report has been submitted and two in-progress review presentations have been given on the interim status of study activities. This document reports the final analysis of treatability evaluations for Area 1595.

Objectives of Study

The intent of this study was to provide hazardous, toxic, and radioactive waste (HTRW) – USAED, Baltimore, and Fort Drum Environmental Public Works with HTRW site-specific information relevant to alternative remediation technologies that is useful in making informed engineering decisions for follow-on remediation activities. To meet this intent, a two-phase treatability study was conducted. Phase I consisted of microcosm evaluations using a single soil core collected in March 1997. Phase II consisted of a side-by-side bench-scale column evaluation comparing natural attenuation, bioventing, and biosparging, using three soil cores collected in July 1997. Specific objectives of this study are to:

- a.* Determine potential microbial activity of Area 1595 subsurface soils.
- b.* Determine intrinsic total petroleum hydrocarbons (TPH) degradation potential of Area 1595 subsurface soils.
- c.* Determine parameters that will enhance subsurface microbial growth in Area 1595.
- d.* Generate data for design and preliminary cost evaluation for remediation of Area 1595.

Description of Site

Fort Drum Military Installation is located in upstate New York, approximately 16 km (10 miles) northeast of Watertown, 128 km (80 miles) north of Syracuse, and 40 km (25 miles) southeast of the U.S./Canadian border (Figure 1). As shown in Figure 2, Area 1595 is centrally located in Gasoline Alley. Previously, two 94,600-l (25,000 gal) and one 45,600-l (12,000 gal) underground storage tanks (UST) containing diesel fuel were buried at Area 1595.

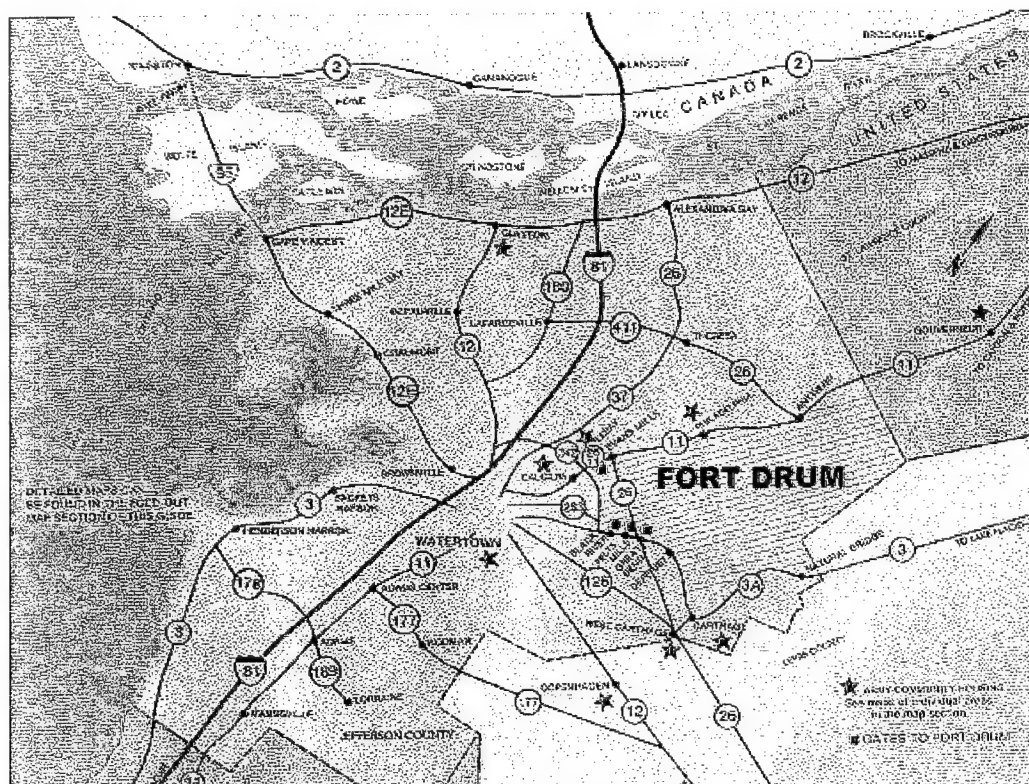


Figure 1. Fort Drum area map

Site background

Area 1595 was used as a fuel storage and dispensing facility from the late 1940s until the mid 1990s. During the early 1970s, a petroleum odor was reported at a spring located northwest and down gradient of Area 1595. The three USTs in Area 1595 were replaced in 1975, at which time a 2.5-cm (1-in.) hole was discovered in one of the USTs. Fueling activities were discontinued in 1994, and the fuel dispensing equipment was removed in 1995.

No documented estimates exist concerning the volume of product released. Fort Drum initiated a product containment and recovery program by constructing a surface water impoundment around the spring and skimming product from the surface of the impoundment. An estimated 26,500-l (7,000-gal) of product had

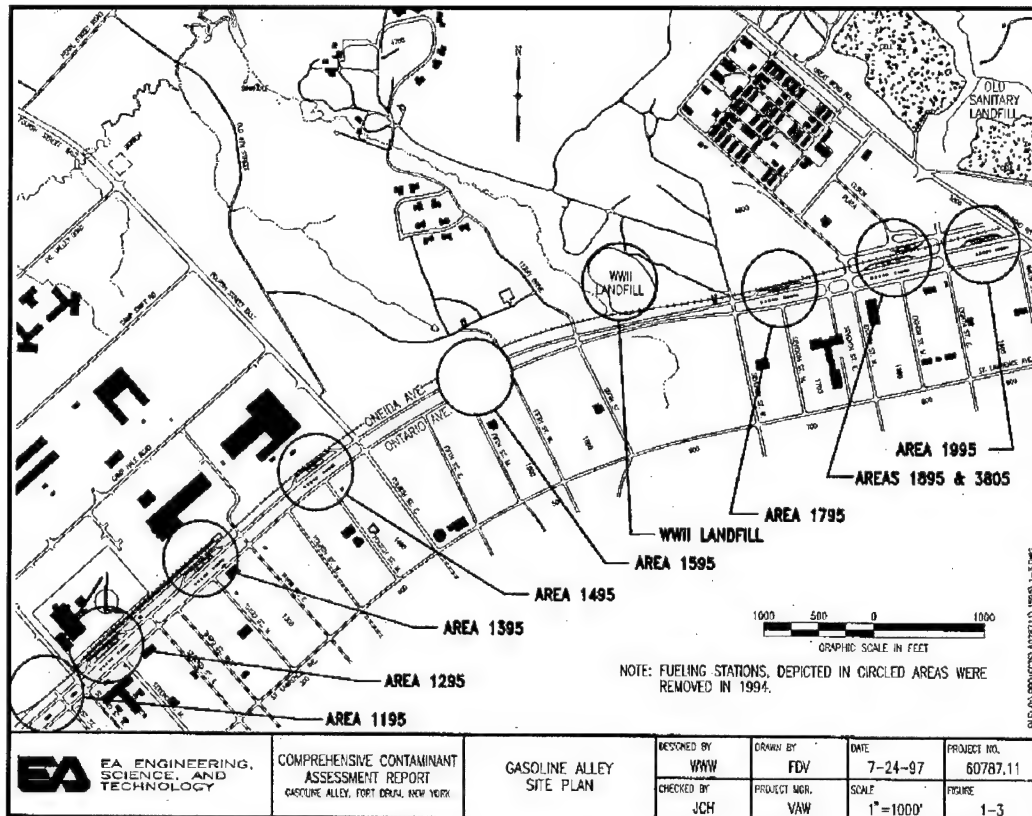


Figure 2. Gasoline Alley

been recovered from the impoundment. Product recovery has continued since that time. However, the only significant report of product removal is 380 l (100 gal) on 5 April 1994.

Site characterization

A separate-phase product released from the former Area 1595 fueling facility remains in the subsurface in the immediate vicinity, and down gradient of the former UST locations. A separate-phase product layer exists above the water table and has been reported in six wells since 1995. Based on the results of a bail-down test, and the sporadic occurrence of product layers in wells, it is postulated that the volume of recoverable product is small.

Movement of the product layer, caused by seasonal fluctuations of the water table, is believed to have created a "smear zone" of petroleum contaminated soil. This contaminated zone may be a source of dissolved-phase contaminants to groundwater moving through the area. Consequently, a plume of contaminated groundwater extends down gradient of the surface water impoundment.

Most of the groundwater contamination exists in the upper-most portion of the shallow aquifer. The depth of the unconsolidated sand aquifer is approximately 11 m (35 ft), but the depth varies throughout the site. Although

contamination has also been reported in deep monitoring wells screened at the bottom of the surficial aquifer, the concentration of chemicals of concern (COCs) are one to two orders of magnitude lower than reported at the shallow wells at the same locations.

The most frequently reported COCs in groundwater are benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, and other petroleum-related hydrocarbons. Chlorinated toluene and benzene isomers have also been reported at locations corresponding to the highest concentrations of petroleum hydrocarbons. High concentrations of iron, manganese, and lead have been reported in various media, with the lead generally reported in association with high concentrations of petroleum hydrocarbons.

High concentrations of BTEX have been reported in surface water samples collected from the Area 1595 Creek, immediately downstream of the impoundment. High concentrations of several polycyclic hydrocarbons (PAHs) have been reported in sediment samples collected from the same area. The extent of surface water and sediment contamination of the Area 1595 Creek is coincident with the area of groundwater and subsurface soil contamination, indicating that discharge of contaminated groundwater is a continuing source of COCs to the creek.

The geometry and areal distribution of the shallow groundwater BTEX plume are primarily influenced by the discharge of groundwater to the surface water impoundment and the Area 1595 Creek, and by several processes collectively known as natural attenuation. These processes include microbially-mediated oxidation of BTEX and other organic compounds. Geochemical data collected since December 1996 indicate that dissolved oxygen and ferrous iron are utilized within the plume area as terminal electron acceptors, facilitating the attenuation of organic compounds.

Several values were reported for the hydraulic conductivity of the surficial aquifer at Area 1595. The logarithmic mean of the hydraulic conductivity from well slug test was found to be 48 ft day^{-1} . Values of hydraulic conductivity calculated during a constant-rate aquifer test were 70.78 and $62.21 \text{ ft day}^{-1}$ by the Cooper-Jacob and Theis methods, respectively. The average hydraulic conductivity calculated by the Quick Neuman solutions from the restart of the Building 1599 treatment system was $32.50 \text{ ft day}^{-1}$.¹

Collection of Soil Cores and Groundwater

Soil

Soil cores were extracted from Area 1595 on two occasions. In March 1997, one core was extracted near well OBG3 and used for chemical and biological characterization of the subsurface and for microbiological assays. This

¹ EA Engineering, Science, and Technology. (1997). *Comprehensive contaminant assessment report – Volume III, Area 1595, Gasoline Alley, Fort Drum, New York.*

information is the focus of Phase I of this report. In July 1997, three additional cores were extracted for use in the bench-scale column treatability study described in Phase II of this report. Each of these cores was extracted within a 3-m (10-ft) radius of the original core extracted in March 1997. The site for core extraction was determined jointly by the USAED, Baltimore, and EA Engineering personnel based on results from the Comprehensive Contaminant Assessment Report for Area 1595 and site worker knowledge of recent sampling events.

Soil cores were extracted using a drill rig with a split-spoon sampler (Figure 3). These cores spanned a continuous depth to approximately 5-m (15 ft) below the ground surface (bgs) reaching several feet below the groundwater table. Site personnel indicated that the groundwater table was at a depth of 4 m (12 ft) at the location and time of core extractions. Soil was collected in acetate liners approximately 2-m (6 ft) in length located inside the split-spoon sampler. Each acetate liner was capped and sealed with paraffin wax when brought to the surface (Figure 4). Cores were placed in a refrigerated trailer at 4 °C and shipped to ERDC.

Groundwater

Groundwater samples were extracted in March 1997 in conjunction with initial subsurface core sampling activities. Groundwater was collected from well 1595-OBG3 (Figure 5). Groundwater and soil cores were stored in 189 l (50-gal) containers and were kept at 4 °C until their use in one of the treatability studies.



Figure 3. Drilling rig

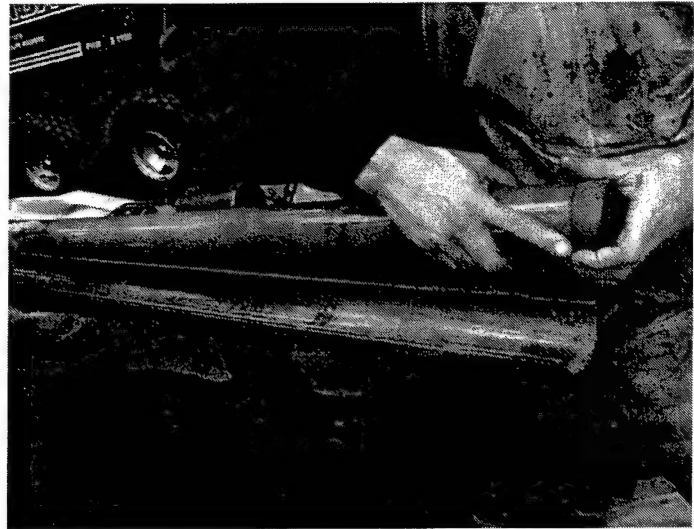


Figure 4. Soil core in acetate liner

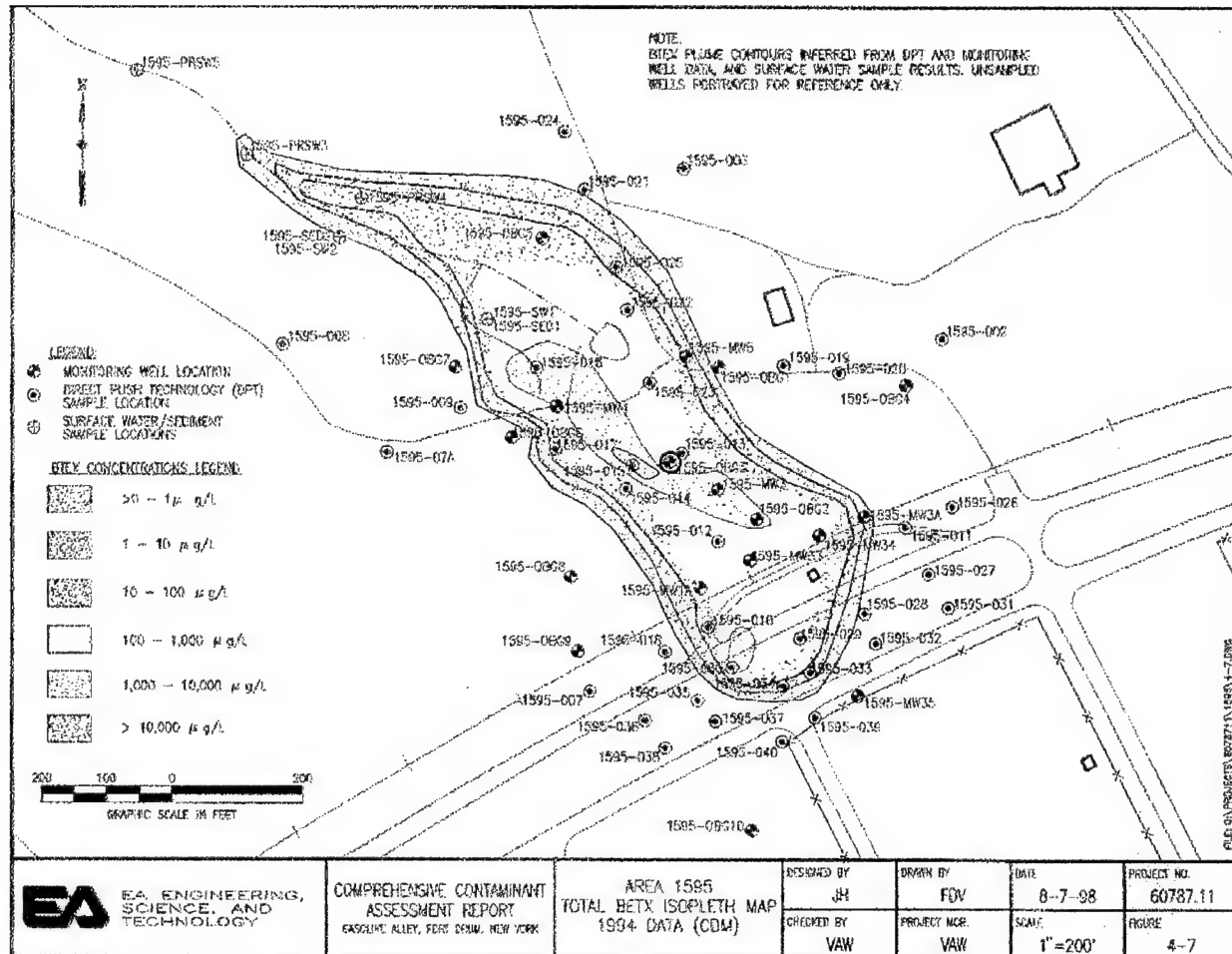


Figure 5. Location of well 1595-OBG3 (circled in red) for groundwater and soil cores

2 Phase I—Microcosm-Scale Evaluation

Background

Respirometry flask studies can be used to: (a) evaluate potential for microbial activity, (b) evaluate potential for degradation of contaminant of concern by native consortia, (c) screen available treatment options, and (d) refine the objectives of larger scale treatability studies. The screening work at the microcosm scale (< 250 mL) provides data necessary for making informed decisions prior to initiating larger scale, more expensive evaluations. In addition, the small scale of microcosm studies allows replications to be conducted for each condition tested.

Objectives of Phase I

The primary objectives of this phase of the evaluation were to:

- a.* Develop a vertical profile of TPH contamination.
- b.* Determine the vertical distribution of viable microbial populations.
- c.* Determine basal microbial activity of native consortia in subsurface soils.
- d.* Determine the intrinsic potential of native consortia to degrade TPH.
- e.* Determine parameters that will enhance degradation of TPH in the subsurface.

Experimental Approach

A continuous vertical subsurface soil core extracted from Area 1595 in March 1997 was chemically characterized for contaminant concentration and biologically characterized for microbial biomass and community structure. Soil samples were removed from the core. TPH contamination and cell membrane lipids (phospholipid fatty acids (PLFA)) were removed from the soil samples by

solvent extraction. Extracts were analyzed by gas chromatography and mass spectrometry. The resulting chemical and biological profiles were compared so that discernable relationships between contaminant distribution and microbial community could be determined.

The basal microbial metabolic activity potential of subsurface indigenous microorganisms was determined by radio-respirometry assays using ^{14}C -labeled acetate. Acetate was chosen for this challenge because it can be easily utilized by most microorganisms as a source of energy and/or carbon. Mineralization of acetate was considered unequivocal evidence of microbial respiration.

Phenanthrene was chosen as a challenge to determine the potential of native microorganisms to degrade TPH. Phenanthrene has a low volatility relative to other fuel-range hydrocarbons resulting in greater analytical recovery. Phenanthrene is also relatively recalcitrant when compared with other fuel-range hydrocarbons, and therefore degradation results will represent conservative estimates of overall microbial activity on bulk hydrocarbon contamination.

The intrinsic ability of soil microflora to mineralize petroleum hydrocarbons was established in two ways. Mineralization of ^{14}C -labeled phenanthrene in radio-respirometry assays established microbial respiration using phenanthrene. Comparison of initial and final concentrations of contaminant in respirometry flasks established overall contaminant degradation during the experiment.

Methods and Materials

TPH and PLFA analytical methods for soil

TPH and PLFA in the soil sample were recovered by extracting 1 g of soil in 3.5 ml of an organic solvent solution consisting of methylene chloride, methanol, and aqueous phosphate buffer in the proportions 5:10:4 on a volumetric basis. The soil solvent mixture was sonicated for 2 min and allowed to equilibrate for a period of 3 hr at room temperature. Following the extraction, 1 ml of methylene chloride and 1 ml of water were added to the solution. This resulted in a two-phase separation consisting of a nonpolar phase containing organic lipids and an aqueous phase. The nonpolar phase was recovered and passed through a pre-packed silica-gel column containing 0.5 g silica gel. To further separate the nonpolar materials, the column was then washed sequentially with 5 ml methylene chloride (extracting petroleum hydrocarbons), 5 ml acetone, and 5 ml methanol (extracting lipids). Each eluted solvent was collected separately for analysis.

TPH quantification was performed by injecting 1 μl of the methylene chloride recovered from the silica gel column on an HP-6890 gas chromatograph (GC) equipped with an SPB-5 capillary column (60m, 0.32mm ID, 0.25 μm film). The column temperature program was as follows: 50 °C for 2 min, increased to 310 °C at a constant rate of 4 °C per min, and then held at 310 °C for 3 min. A 1-min splitless injection was used at a purge of 80 ml/min. The injector was maintained at 250 °C and the flame ionization detector at 320 °C. Nonadecanoic

acid methyl ester at 50 pmole/ μ l was used as an internal standard. An internal standard calculation was used to convert total peak area between retention times of 10 and 50 min into TPH concentration. Reproducibility of the gas chromatographic analyses averaged a standard error of 9 percent while replicate analyses of soil extracts (1-g size) averaged a standard error of 15 percent for the soil column soils. The range of error was much greater for the soil analyses where a minimum error of 5 percent and a maximum error of 39 percent were seen. In both phases of this evaluation, an estimated standard deviation of 20 percent was assumed for all soil sampling points where only one sample was taken.

TPH. TPH recovery from the soils in this experiment, by the method described above, was 58 ± 5 percent. Soil TPH values reported in this study are for the recoverable TPH (rTPH). rTPH values are not corrected to include that fraction of the TPH in the soil which is not recoverable. Recovery of TPH from a clay reference soil, by the method described above, was approximately 85 percent, which is a more typical value. An independent analysis of soil samples was performed by Argus Analytical, Inc., Jackson, MS. Recovery percentages and rTPH concentrations determined by Argus Analytical, using the U.S. Environmental Protection Agency (EPA) Method 3550 for soil extraction and EPA Method 8015¹ for analysis, correlated well with the results obtained by the method described in Table 1. Because recovery of petroleum hydrocarbons from a sandy soil are usually high, the low recovery from the sandy Fort Drum soils suggests that something other than a normal sorption process of the petroleum hydrocarbons to the soil particles is affecting the recovery of TPH.

Table 1
rTPH Analytical Method Comparison

Sample Location	Depth m bgs ft bgs	WES Bligh-Dyer Extraction, mg/kg	WES EPA Method (s.d.), mg/kg	Argus Labs, Inc. EPA Method, mg/kg
1595	3.2 (10.5)	507	483 (73)	158
	3.5 (11.5)	13,369		13,700
1795	2.9 (9.5)	50	4750 (789)	36
	3.7 (12.0)	1,924		154
3805	6.7 (22.0)	17	4 (4)	35
	9.6 (32.0)	14		0

Notes: bgs denotes below ground surface; s.d. denotes standard deviation.

PLFA. The methanol fraction recovered from the silica gel column was dried under nitrogen and then subjected to transesterification in mildly alkaline methanol to form methyl esters of the ester-linked PLFA. PLFA were identified and quantified on an HP-5973 mass selective detector interfaced to an HP-6890 GC. The GC was equipped with a J&W DB-5ms capillary column. During each injection, the column temperature was held at 80 °C for 2 min, increased to 150 °C at a constant rate of 10 °C per min, then increased to 282 °C at 3 °C per min, and held at 282 °C for another 2 min. A 2-min splitless injection of 1 μ l at a

¹ USEPA. (1992). "Test methods for evaluation of solid waste physical/chemical methods," SW-846, Office of Solid Waste and Emergency Response, Washington, DC.

purge of 80 ml/min was used. The injector was maintained at 270 °C. Mass spectra were collected at 70 electron volt using positive electron impact.

Microcosm flask setup

Respirometry flasks (250-ml) from Reliance Glass were used for the microcosm studies (Figure 6). Flasks were acid washed, dried, and rinsed with 5 to 10 ml dichloromethane and air dried in a Biofree clean hood. Flasks, caps, and hydroxide wells were sealed with aluminum foil and double autoclaved. Aliquots of soil were placed into the flask and challenged with radio labeled tracer compound. Flasks were equipped with center wells that contained 2-ml of a 1-normal potassium hydroxide solution. As a result of mineralization of ^{14}C -labeled acetate or ^{14}C -labeled phenanthrene, $^{14}\text{CO}_2$ was trapped as carbonate in the hydroxide solution. The hydroxide solution was removed from the well using a syringe or a pipette at regular intervals (based on rate of microbial respiration) for analysis by a Hewlett Packard liquid scintillation counter (LSC). Fresh hydroxide solution was placed in the well immediately after withdrawing the used hydroxide solution.



Figure 6. Example respirometry flask

Results and Discussion

Data developed from Phase I are included in Appendix A.

Vertical distributions of rTPH and microbial characterization

The distribution of rTPH and microbial biomass (PLFA estimates) along the depth of the soil core are presented in Figure 7. The contaminant concentrations are low near the ground surface and increase with depth. When aquifer levels are approached at approximately 3.2 m (10.5 ft), the contaminant concentration rapidly decreases to levels similar to surface soils. Site personnel indicated the smear zone at Area 1595 to be between 3.2 and 3.5 m (10.5 and 11.5 ft). The general subsurface contaminant concentration profile is characteristic of many hydrocarbon contaminated sites with a notable exception, the significant dip in the contaminant concentration profile at the top of the smear zone. At 3.5 m (11.5 ft), the concentration peaks at approximately 1,200 ppm. The low contaminant concentration at 3.2 m (10.5 ft), bounded on top and bottom by higher contaminant concentrations, suggests possible contaminant microbe interaction.

A conversion of membrane lipid content to cell numbers showed the soil to contain approximately 4×10^8 cells g^{-1} at the ground surface which is a typical

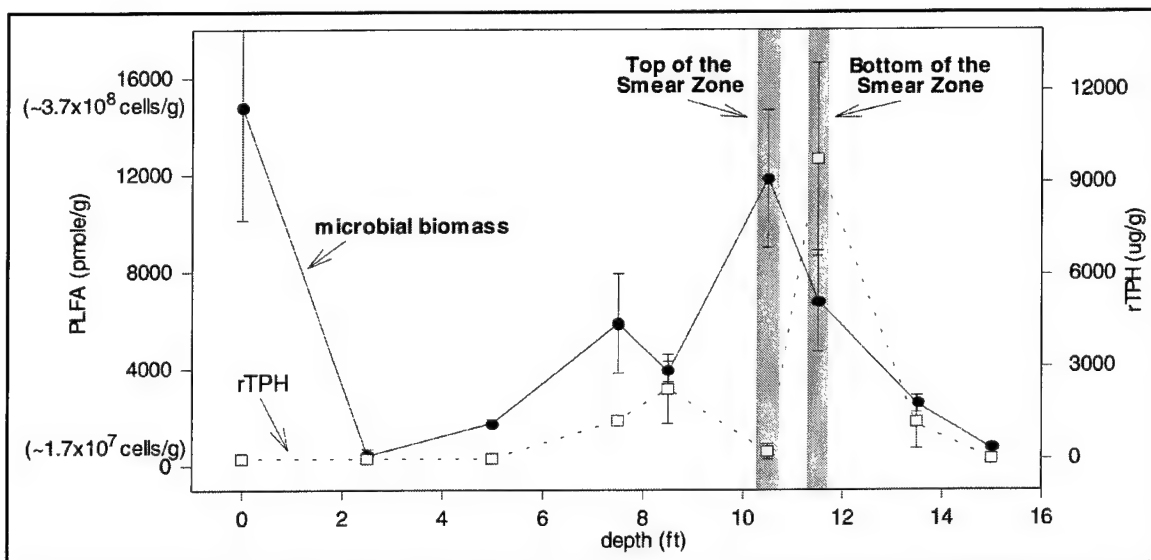


Figure 7. Vertical profile of rTPH vs viable biomass (PLFA)

value for ground surface biomass levels. Typical subsurface biomass profiles show an order of magnitude decrease within the first 0.3 to 1.5 m (1 to 5 ft), followed by another order of magnitude decrease by the 3- to 15-m (10- to 50-ft) depth. Although microbial biomass in the soil core decreased by an order of magnitude in the first 0.9 m (3 ft) below the surface, biomass levels at a depth of 3.2 m (10.5 ft) were similar to that at the surface. The finding of biomass levels at a depth of over 1.5 m (5 ft), which are similar to surface soil levels, suggests a contaminant influence on microbial growth.

Microbial community

In addition to determining microbial abundance, specific lipid biomarkers are used to determine microbial community composition. Figure 8 illustrates the relationship of the vertical contaminant and microbial community profiles. From this graph, a coincidence at the 3.2-m (10.5-ft) depth can be seen between the decrease of petroleum hydrocarbon contamination and an increase in the ratio of micro-eukaryotic organisms, known petroleum-degrading microorganisms.

An examination of the in situ microbiota revealed the presence of a distinct microbial community, which contained descriptive characteristics that correlated significantly with in situ measures of contaminant biodegradation. Exploratory statistical analysis of the membrane lipid (PLFA) profiles, which reflect microbial community structure, revealed the presence of three distinct or unique microbial communities within the depth profile. rTPH concentrations associated with two of the communities (i.e., deeper subsurface samples) were greater than the third community (i.e., near-surface samples). Although the level of viable biomass was not significantly different among the three distinct communities, the ratio of viable biomass to rTPH was considerably greater in one of the three

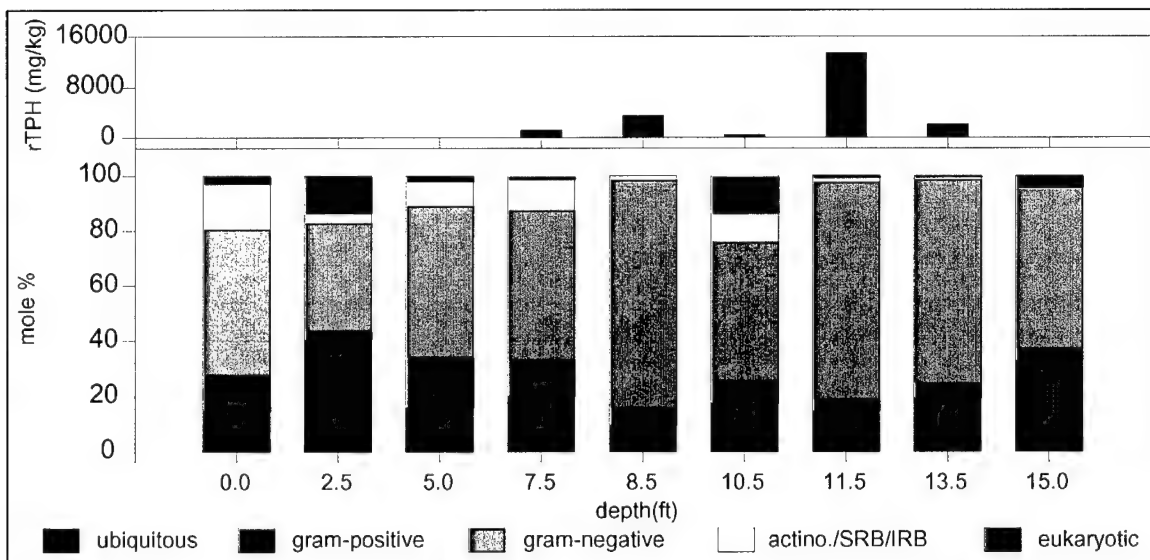


Figure 8. Vertical contaminant and microbial community profile

communities, the one typified by the near surface samples as well as the top of the smear zone. This result suggests that a biodegradation potential (i.e., substantial viable biomass and lower rTPH concentration) is associated with this community. In situ evidence of the biodegradation potential (or a confirmation of this assumption) was found in the ratio of specific n-alkane (readily degradable) to highly branched alkane (recalcitrant) moieties within the TPH contamination. The community identified as having the highest biodegradation potential produced the lowest mean value of this ratio for the three communities identified. The identification of a selective loss of a readily utilizable substrate relative to a more recalcitrant one in situ, with direct relationships to microbial community structure, indicates the occurrence (or supports the assumption) of in situ biodegradation activity.

Significant differences in the mean percentages of gram-positive, micro-eukaryotic, and actinomycete (actino.)-like bacterial groups (estimated from the relative percentages of PLFA biomarkers) were observed between the three distinct communities described above. The identified biodegradation community contained the greatest percentages of micro-eukaryotic and actinomycete PLFA biomarkers. In these soils, the biomarker results suggest that the micro-eukaryotic group is largely comprised of fungi. A number of fungi, especially *Penicillium* and *Cunninghamella*, have had a degrading effect on petroleum hydrocarbons. This community also showed the greatest mean percentage of gram-positive bacterial PLFA biomarkers. The gram-positive *Arthrobacter* species have frequently been isolated from petroleum contaminated soils and sediments. Both of these bacterial groups, micro-eukaryotic and gram-positive, showed significant negative correlations with rTPH concentration.

In contrast, the community showing the least evidence of an in situ biodegradation potential (based on measures described above) contained the greatest percentages of PLFA biomarkers descriptive of sulfate reducing bacteria

(SRB) and/or iron reducing bacteria (IRB). The measure of this bacterial group was also found to correlate positively (and significantly) with rTPH concentration. Redox potentials, and associated microbial induced reactions, often follow a pattern whereby oxidation of carbon is followed by the reduction of molecular oxygen, nitrate, ferric hydroxide, and then sulfate. This pattern is typically seen from outside to inside of a contamination plume. The occurrence, in Area 1595 subsurface soils, of increased biomarker percentages indicative of obligate anaerobes where rTPH concentrations are highest is not atypical. Although anaerobic biodegradation of petroleum hydrocarbons has been demonstrated, the process is often negligible in light of the aerobic biodegradation potential. Two other key characteristics could be associated with this community; increased values for an environmental stress biomarker and a decrease in diversity. Both characteristics suggest a microbial response to the contamination.

The PLFA biomarker analyses indicated that gram-positive bacterial and fungal input was associated with the identified in situ biodegradation potential and that anaerobic micro-niches likely existed in the center of the contaminant plume.

Acetate challenge respirometry

After validating the existence of potentially viable microorganisms in the subsurface of Area 1595 at the top and the bottom of the smear zone, a series of respirometry flask evaluations were conducted to establish the catabolic potential of the existing microorganisms. Table 2 shows the experimental design for the ^{14}C -acetate challenge.

Table 2			
Experimental Design for Tracer Acetate Challenge			
Upper Smear Zone		Lower Smear Zone	
Saturated	Unsaturated	Saturated	Unsaturated
X	X	X	X
Note: All evaluations conducted in triplicate.			

Respiration was determined through periodic analysis of hydroxide $^{14}\text{CO}_2$ traps by a liquid scintillation counter (LCS). Results displayed in Figure 9 validate the basal metabolic potential of Area 1595 subsurface microorganisms. In both saturated and unsaturated evaluations, the microorganisms from the top of the smear zone (3.2 m (10.5 ft)) demonstrated enhanced microbial activity. Appendix A presents ^{14}C - CO_2 recovery data from the acetate challenge.

Phenanthrene challenge respirometry

Experimental treatments for this evaluation (Table 3) were selected to simulate plausible full-scale in situ remediation strategies, including the addition

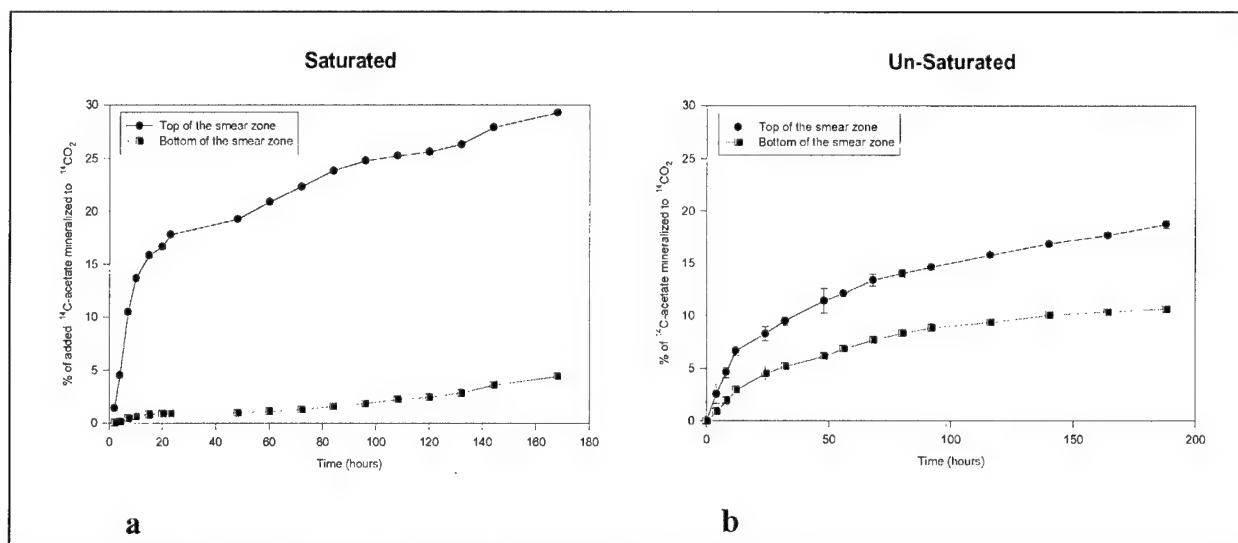


Figure 9. Respirometry results of acetate challenge

Table 3
Experimental Design for Tracer Phenanthrene Challenge

	Upper Smear Zone		Lower Smear Zone	
	Saturated	Unsaturated	Saturated	Unsaturated
Sterile Control	X	X	X	X
Control (Head Space Air)	X	X	X	X
Nutrient	X	X	X	X
H ₂ O ₂	X	X	X	X
H ₂ O ₂ + Nutrient	X	X	X	X

Note: All evaluations conducted in triplicate.

of hydrogen and the addition of nutrient amendments. Hydrogen peroxide was chosen as a method of oxygen delivery because of its ability to maintain desirable oxygen concentrations in groundwater further from the source well than sparging with air or oxygen. Hydrogen peroxide was added to the flask at a concentration of 4.76 mg per gram of soil. This concentration was demonstrated to be beneficial to aerobic microorganisms in previous studies conducted at ERDC. Nutrient solution, MiracleGro[®], was added at a concentration of 8.4 mg per gram of soil. MiracleGro[®] used in this study contained 7 percent total nitrogen (0.4 percent ammoniacal and 6.6 percent urea), 7 percent available phosphate (P₂O₅), and 7 percent soluble potash by weight. The added concentration of each nutrient to the flasks was therefore 0.59 mg per gram of soil.

Results of the phenanthrene challenge are shown in Figure 10. Appendix A represents ¹⁴C-CO₂ recovery data for the phenanthrene challenge. In general, addition of amendments to the subsurface soils did not improve the catabolic

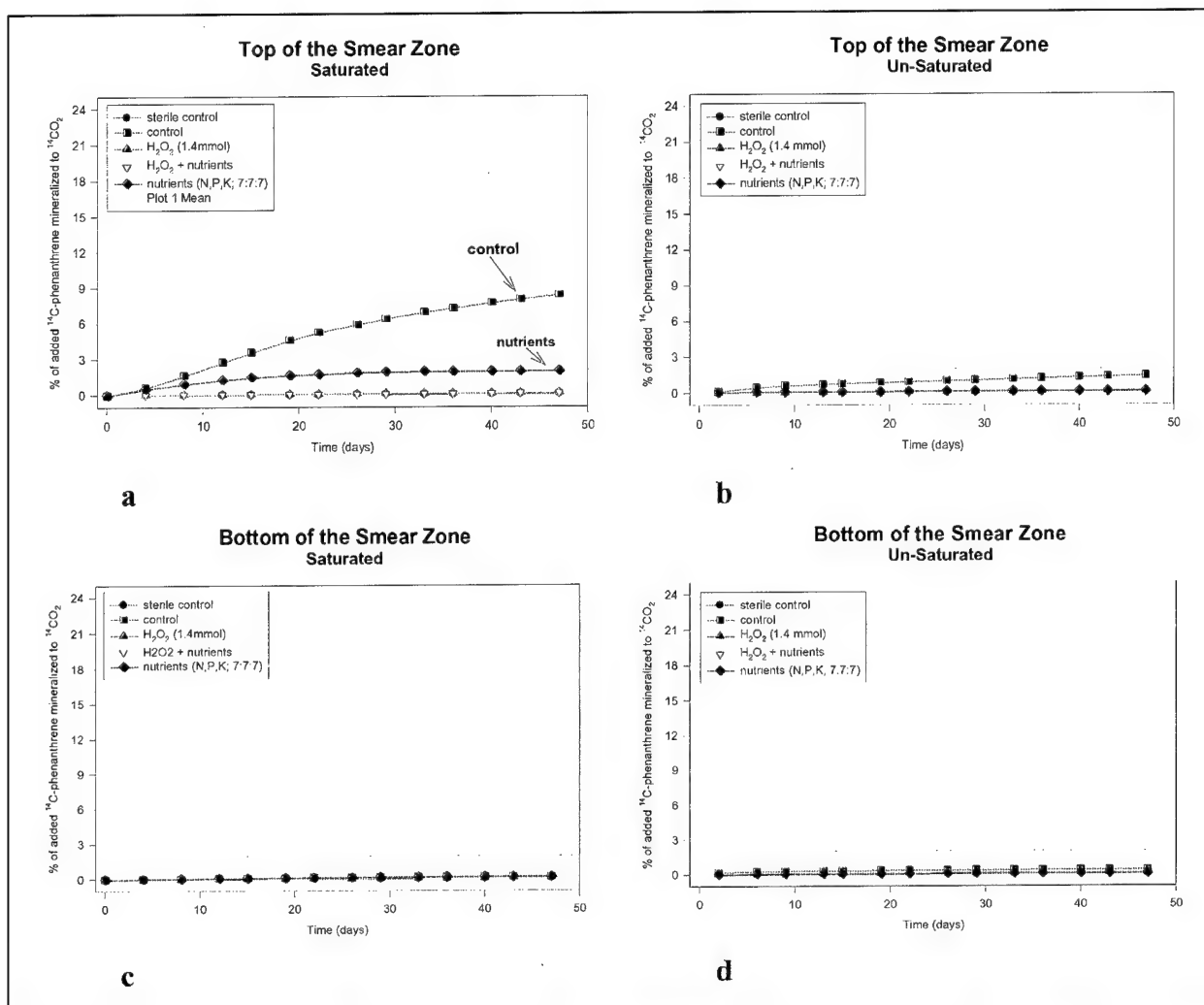


Figure 10. Respirometry results from phenanthrene challenge

activity of the microbiota from Area 1595. The only condition showing significant mineralization of ^{14}C -phenanthrene was the control with soil from the top of the smear zone under saturated conditions. In this case, oxygen from atmospheric air in the headspace of the flask stimulated degradation of phenanthrene. Subsequent to the analysis of ^{14}C -phenanthrene, rTPH analysis was performed on the entire final contents of the flasks from the sterile control and control with no amendments conditions. The rTPH analysis indicated $1,276 \pm 388$ and $1,020 \pm 180$ μg rTPH per gram soil for the sterile control and control flasks, respectively. This indicates that in addition to the mineralization of phenanthrene in the control flask, a 20 percent greater reduction in the total rTPH was seen in the control flask when compared to the sterile control.

Conclusions from Phase I

Although the presence of viable microorganisms is essential to any successful bioremediation effort, biomass must also have the capacity to actively metabolize the contaminant. An initial screen was performed on soils recovered from the subsurface core collected from Area 1595. Microorganisms from soils recovered from the top and bottom of the smear zone were determined to exhibit characteristics suggesting a capability for degrading petroleum hydrocarbons. Microorganisms in soil samples from the 3.2-m (10.5-ft) depth were capable of mineralizing ~37 percent of ^{14}C -acetate to $^{14}\text{CO}_2$ in 12 days. This demonstrated that the increased subsurface biomass at 3.2 m (10.5 ft) was capable of utilizing the added substrates.

The extant microbiota identified in the initial screen of Area 1595 soil core were challenged with uniformly labeled ^{14}C -phenanthrene. Nutrient and hydrogen peroxide amendments were included to determine their effects on bioremediation. Microbiota from soils taken from the top of the smear zone (3.2 m (10.5 ft)) demonstrated the ability to mineralize phenanthrene utilizing only oxygen from the headspace of the flask. Nutrient and hydrogen peroxide amendments did not enhance the degradation of phenanthrene and may have hindered the degradation of phenanthrene. Although the recalcitrant contaminant was not demonstrated to be readily mineralized, in situ evidence of n-alkane utilization was observed.

Experimental results from Phase I indicate biological remediation of subsurface contamination at Area 1595 is a viable alternative based on the following:

- a. Subsurface microbial populations were on the order of 10^5 to 10^8 cells per gram soil, approaching biomass levels observed in healthy topsoil.
- b. Biomass populations demonstrated the ability to mineralize acetate during the screening respirometry evaluation.
- c. Biomass populations demonstrated the ability to mineralize phenanthrene during a 47-day radiotracer challenge evaluation.
- d. Coincident with phenanthrene mineralization, sacrificial respirometry flasks analysis resulted in a ~20 percent decrease in the mean rTPH concentration in soil.
- e. Highly significant correlation was measured between total biomass, specific microbial populations associated with hydrocarbon degradation, and TPH concentration suggesting the active degradation of available contaminant.

3 Phase II–Bench-Scale Column Studies

Objectives

The objectives of Phase II of this study were to provide HTRW – USAED, Baltimore, and Fort Drum Environmental Public Works with site-specific data relevant to alternative remediation technologies that are useful in making engineering design decisions and preliminary cost estimates. To meet this objective, bench-scale soil-column studies were conducted using three soil cores from Area 1595 of Gasoline Alley. These column studies were used to produce a side-by-side evaluation of bioventing, biosparging, and natural attenuation treatment alternatives for Area 1595. Because the addition of hydrogen peroxide showed no enhancement of biological degradation of phenanthrene in Phase I of this study, sparging of air in the saturated zone (biosparging) was investigated as a method of oxygen delivery instead of hydrogen peroxide addition.

Experimental Design

The bench-scale soil-columns study was designed to simulate the in situ conditions of the contamination site. To accomplish this, soil columns were kept in a walk-in cooler that was dedicated to this study for the duration of the experiment. The cooler temperature during the study was maintained at 10 °C, the average yearly aquifer temperature for the Fort Drum area suggested by Mr. James Spratt, USAED, Baltimore.

Soil-core material was packed in custom-manufactured glass columns with an inside diameter of 8-cm (3.25 in.) and a height of 1.8-m (6 ft). Acetate liners were cut into approximately 46-cm (18-in.) sections, and the soil was forced out of these sections into the top of the columns. Soil from the liners was added, beginning with the bottom of the core and ending with the top. This packing technique did cause disturbance of the soil but maintained the vertical profile of the soil core. To accommodate the 5-m (15-ft) depth of the cores, two columns were connected in series with 6.4-mm (¼-in.) stainless steel tubing for each core. Sample ports were located at approximately 0.3-m (1-ft) intervals along the length of the column. The inside diameter of the glass columns was larger than that of the acetate liner, which resulted in a reduction of total height between the

soil core and the glass column. A listing of column ports, their depth from the top of soil column, and correspondence with core depth below ground surface is presented in Table 4.

Table 4		
Column Depth vs Core Depth		
Column – Port	Column Depth, cm (in.)	Core Depth, cm (in.)
2-Top	0 (0)	0 (0)
2-58	7 (2.8)	10 (3.9)
2-46	19 (7.5)	26 (10.2)
2-34	31 (12.2)	43 (16.9)
2-23	42 (16.5)	58 (22.8)
2-10	55 (21.7)	76 (29.9)
2-0 & 1-Top	65 (25.6)	90 (35.4)
1-58	72 (28.3)	99 (39.0)
1-46	84 (33.1)	116 (45.7)
1-34	99 (39.0)	137 (53.9)
1-23	107 (42.1)	148 (58.3)
1-10	120 (47.2)	166 (65.4)
1-0	130 (51.2)	179 (70.5)

Each port was sealed with a 25-mm Teflon plug. Plugs used in ports 1-10 and 1-23 were drilled, tapped, fit with two-way valves, and packed with glass fiber. These ports were used for taking water samples. The plug used in port 1-34 of the bioventing column was fit with a tubing connector for connection to airflow tubing. The ends of each column were closed with a 50-mm Teflon plug that was screened with a 50-mm diffuser stone. Each end cap was tapped and fit with a tubing connector.

A schematic of the columns for bioventing and bioparging is shown in Figure 11. Figures 12 and 13 show the actual column setup.

To simulate the saturated zone of the contamination site, groundwater from the site was added through port 1-0 at the bottom of the first column to a height of approximately 81-cm (32-in.).

Forcing breathing-grade air from a pressurized cylinder through specified ports in the respective columns simulated bioventing and bioparging. For bioparging, the air was forced in port 1-0 located in the column end cap. This location was at the bottom of the simulated saturated zone. For bioventing, the air was forced into the center of the column through stainless steel tubing placed through port 1-34. This location was in the smear zone and was approximately 5-cm (2-in.) above the simulated saturated zone. An on-off valve, mass-flow meter, and check-valve in series controlled the flow of pressurized air into each series of columns. All of the ports in the bioventing and bioparging columns were tested and ensured for absence of air leaks.

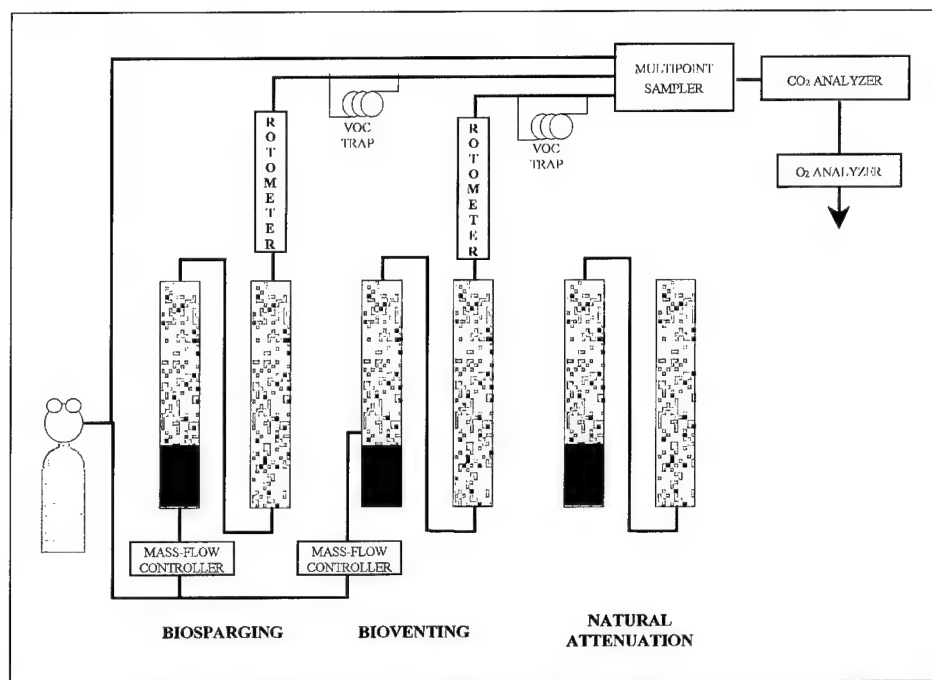


Figure 11. Column design (VOC – volatile organic carbons)

The desired airflow rate of 1 standard cubic centimeter per minute (sccm) was calculated using the guidance given in the EPA Manual.¹ A higher flow rate (4sccm) was also used in both the biosparging and the bioventing columns to determine the effect of airflow rate in excess of the EPA recommendations and to give an unbiased comparison between the two treatment methods. Airflow was delivered in a continuous stream to the columns except during sampling periods at which time the airflow was halted. Airflow through the columns was initiated at 4 sccm was maintained for 5 weeks. During the final 4 weeks of the study, the airflow was reduced to the calculated EPA recommendation of 1 sccm. No air was forced into columns simulating natural attenuation in the aquifer.

Methods and Material

Sampling and analysis of off-gases

Air forced through the columns was collected at the exit in Tedlar™ bags and analyzed for oxygen and carbon dioxide concentrations. Air collected in the Tedlar™ bags was periodically drawn from the bags by a multipoint sampler and

¹ USEPA. (1995). EPA Manual – “Bioventing principles and practice – Volume II: Bioventing design,” Washington, DC.

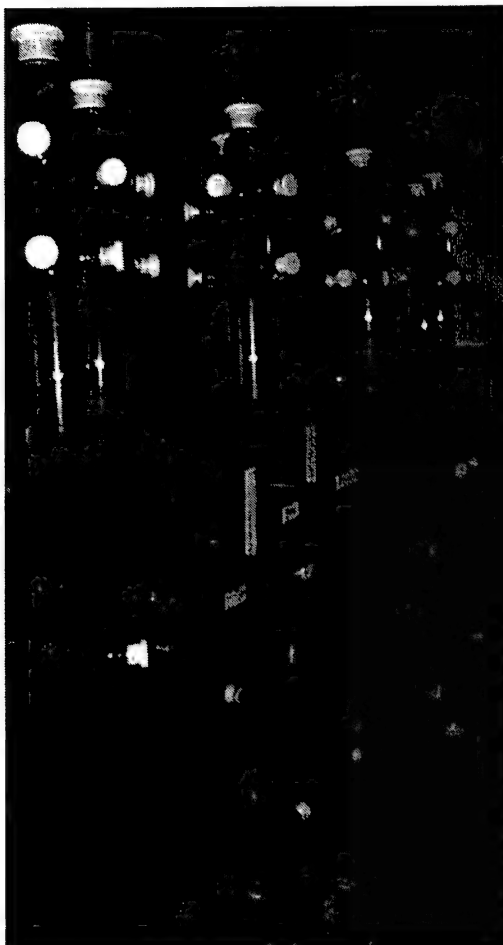


Figure 12. Columns

100 percent (by volume) with a resolution of 0.01 percent and an accuracy of ± 0.01 percent. The Tedlar™ bags were emptied after the completion of each sample period and reused. The exit gas carbon dioxide data were logged automatically into a computer, shown in Figure 14. Oxygen and carbon dioxide analyses could not be performed for the natural attenuation columns, since no air was forced through these columns.

Analysis of VOC in the off-gases from the columns was attempted. Air exiting from the bioparging and bioventing columns was passed through TENAX traps for a known amount of time. These traps were then extracted and the extract analyzed by gas chromatography for VOCs. Because there was no airflow through the natural attenuation columns, a VOCARB trap was connected to the headspace at the top of the soil column for a known amount of time, approximately 2 weeks. The VOCARB trap was then analyzed by gas chromatography. However, analysis of the data from all columns indicated that the traps were being saturated, and therefore reliable volatilization rates could not be calculated.

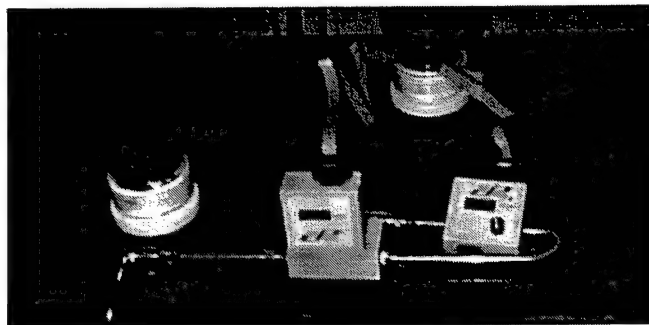


Figure 13. Flow control

passed sequentially through a photoacoustic infrared multi gas analyzer, a fuel-cell-type oxygen detector, and then exhausted. The multigas analyzer was used for measurement of CO₂ concentration in the exit air. The multigas analyzer had a minimum CO₂ detection limit of 13 parts per million (by volume), a detection span of five orders of magnitude, and a resolution of 0.01 ppm. The accuracy of the instrument in the calibration range for this study was ± 10 ppm. The multigas analyzer also measured and compensated for the effect of water vapor in the air. The oxygen analyzer measured oxygen concentration from 0.01 to

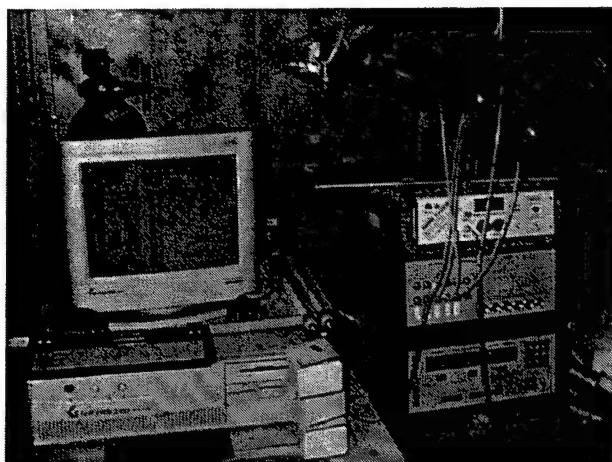


Figure 14. CO₂ and O₂ analytical equipment

Soil and water sampling

Soil and water samples were taken from the columns at specified times. A schedule of sampling is presented in Table 5. Airflow into the bioventing and bioparging columns was stopped approximately 2 hr before each sample period. After water and soil sampling was complete, contaminated water from Area 1595 was added to each column through port 1-0 to return the water level to a height of 81-cm (32-in.) from the bottom of the column. Each sampling event lasted 8 to 12 hr. After each sampling event, airflow in the columns was resumed.

Soil and water sampling method

Water samples were taken from ports 1-23, 1-10, and 1-0 for each set of columns. All the free water was drawn from port 1-23, followed by port 1-10, then port 1-0. By taking samples in this manner, samples from port 1-23 represented the top of the saturated zone, samples from port 1-10 represented the middle of the saturated zoned, and samples from port 1-0 represented the bottom of the saturated zone.

Water sample method. Samples were drawn from the ports by connecting a length of Tygon™ tubing to the valve attached to each of these ports. The valve was opened and the water was drawn through the tubing by an occlusion-type pump directly into sample vials. For each sample port, two 40-ml vials of pore water were collected first, followed by the collection of all remaining water into 125- ml sample bottles. The 40- ml sample vials were collected for the purpose of VOC analysis. To preserve the samples, 0.2 ml, 65 to 80 percent hydrochloric acid (HCl) was added to each vial. The sample vials were filled completely to eliminate headspace when sealed. Samples were stored at 4 °C until their delivery for analysis the following day. The water collected in 125- ml sample bottles was used for analysis of PAHs. These samples were also stored at 4 °C until delivered for analysis the next day.

Soil sampling method. Soil samples were collected after taking water samples. Soil samples were also taken following the sample schedule shown in Table 5. Only the initial and final soil samples were taken from the bottom, port 1-0 and 2-0, of each column because of the difficulty involved in sampling this location. Soil samples from ports 1-Top and 2-Top were also taken only during

Table 5
Sampling Schedule

Date		8/5/97	8/12/97	8/20/97	9/3/97	9/18/97	10/2/97	10/14/97
Days Since Start		0	7	15	29	44	58	70
Days Between Samples		0	7	8	14	15	14	12
Airflow Between Samples		0, sccm	0, sccm	4, sccm	4, sccm	4, sccm	1, sccm	1, sccm
Core ↑ Top ↓ Bottom	Column-Port	2-TOP	S	S				S
		2-58	S	S	S	S	S	S
		2-46	S	S	S	S	S	S
		2-34	S	S	S	S	S	S
		2-23	S	S	S	S	S	S
		2-10	S	S	S	S	S	S
		2-0	S					S
		1-TOP	S	S				S
		1-58	S	S	S	S	S	S
		1-46	S	S	S	S	S	S
		1-34	S	S	S	S	S	S
		1-23	W	S,W	S,W	S,W	S,W	S,W
		1-10	W	S,W	S,W	S,W	S,W	S,W
		1-0	W	S,W	W	W	W	S,W

S – soil sampled

W – water sampled

Note: Aeration rates are for bioventing and biosparging columns. There was no aeration rate for natural attenuation column.

A sample from the barrel of contaminated water used in the study was substituted for water samples shown on 8/5/97. This sample represents the initial water concentration for each treatment period.

The 8/12/97 samples represent the end of the equilibration period.

the second, third, and last sample periods for the same reason. Soil samples collected during the initial and final sample period were approximately 30 grams. Soil samples taken at all other sample intervals were between 1 to 3 grams to minimize the effect of sampling on the behavior of soil columns.

Soil was collected from each port by removing the Teflon plug and collecting the soil sample with a spatula. The soil samples were taken from a location approximately 2.5 cm (1 in.) behind the surface of the soil in each port and placed in sampling jars. After all soil samples were taken, they were placed in a freezer until extractions for rTPH and fatty acids could be performed.

Analytical methods. Water samples were analyzed by EPA Method SW846-8260A for VOCs and by EPA Method SW846-8270B for PAHs.¹ The analytical methods for rTPH and biomass described in paragraph “TPH and PLFA analytical methods for soil,” Phase I, Chapter 1, were used in the column evaluations.

¹ USEPA. (1992). Op. cit.

Results and Discussion

Heterogeneity between the different soil cores

Initial rTPH concentrations at each sample location in the three soil cores (bioparging, bioventing, and natural attenuation columns) are presented in Figure 15. In each case, relatively high rTPH concentrations were found in the bottom half of the cores; the concentrations peaked and then decreased again as the saturated zone was approached. These profiles are qualitatively similar to each other and to the profile observed in the core collected in March 1997 (Figure 7). However, each of these cores is quantitatively different from the others, reflecting the heterogeneous nature of hydrocarbon contamination at this location. Dendritic lines of the rTPH contamination in the soil columns were observed. This type of contamination distribution is common with petroleum-contaminated soil and results in high heterogeneity of rTPH contamination levels on a small areal scale.

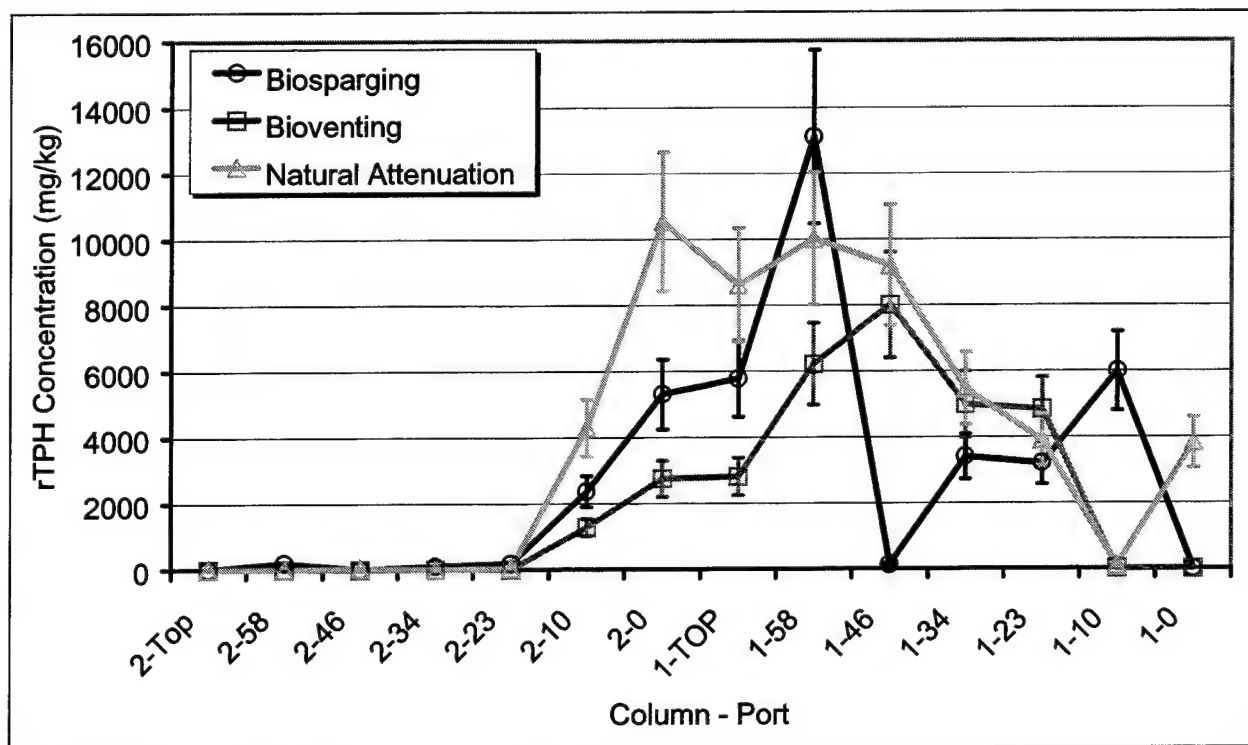


Figure 15. Initial soil rTPH concentrations in Area 1595 cores

The heterogeneity of the cores was evident in terms of microbial analysis also. The estimates of the initial viable biomass (PLFA) from each of the three cores are shown in Figure 16 at each of the sample locations. Again, the cores were collected in close proximity to each other and show large variability.

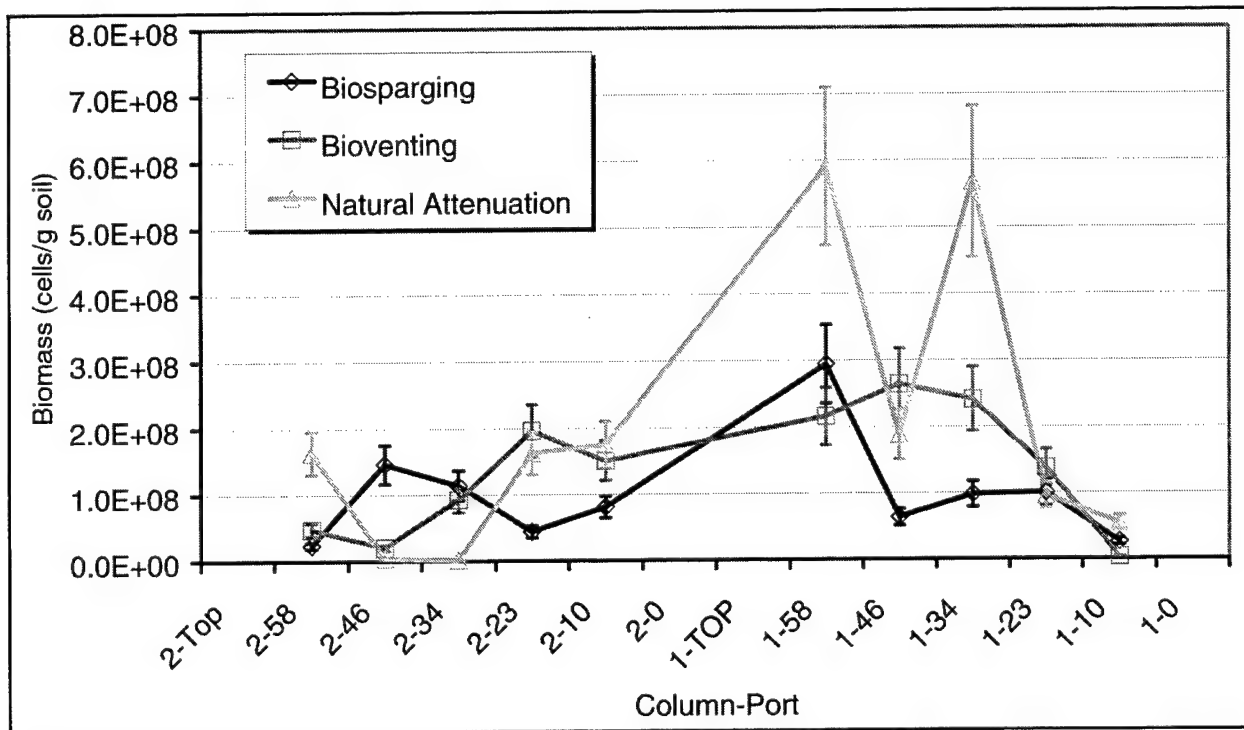


Figure 16. Initial biomass analysis Area 1595 cores

Natural attenuation

All data developed from the natural attenuation column is provided in Appendix B.

Soil phase rTPH and biomass concentrations. The TPH concentration profiles in the natural attenuation column at the beginning and at the end of the experiment (10 weeks) are shown in Figure 17. On the whole, the rTPH profile in the column remained unchanged over this time period. The small differences between the concentration profiles at all locations can be attributed to analytical uncertainty.

The total rTPH present in the column at the beginning of the experiment was 104.6 g ($\sigma = 20.9$). rTPH in the column at the end of the 10-week evaluation was measured to be 86.3 g ($\sigma = 17.3$). These data were based on analysis of 30-g samples of soil collected from each port (Table 5) at the beginning and end of the experiment. It can only be said with 75-percent confidence that these numbers are different from each other, suggesting that the losses of rTPH over 10 weeks under conditions of natural attenuation are not discernible. Analyses of 1-g intermediate point samples resulted in significantly larger variations in the total amounts of rTPH in the column, and no trend could be seen.

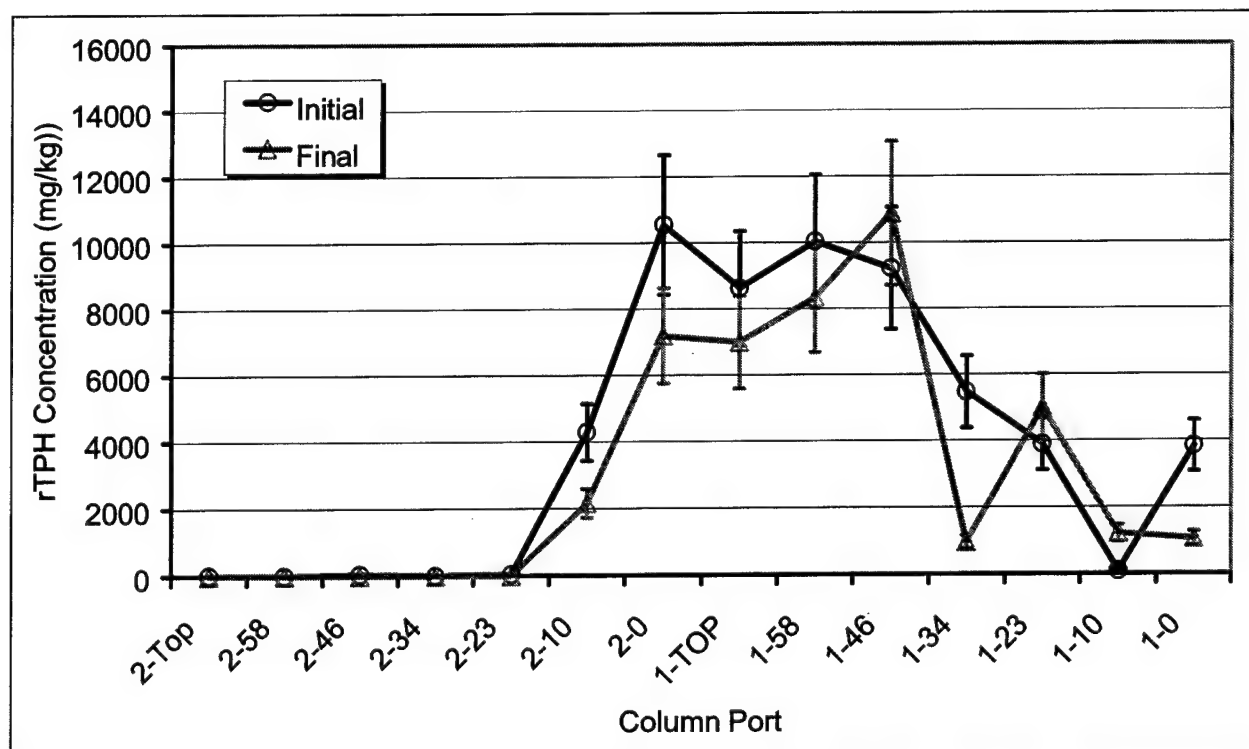


Figure 17. Initial and final rTPH contaminant profile – natural attenuation

The biomass concentration profiles at the initial and end points of natural attenuation experiment are shown in Figure 18. Here too, there was no significant change in the total biomass observed in the column.

Aqueous phase rTPH concentrations. Total petroleum concentration in water samples from the bottom, middle, and top of the saturated zone are illustrated in Figure 19 for each treatment period and listed in Table 6. As identified earlier, the saturated zone was drained at the end of each sampling period as described in the paragraph “Water sampling method” of Phase II, Chapter 2. Contaminated groundwater from the site was then added to the column. This water sampling method simulated the movement of groundwater through a specified aquifer zone and avoided cross contamination between the various column levels during water sampling. Any change in the aqueous contaminant concentration during a treatment period is the cumulative result of interactions between groundwater and contaminated soil, and of any biotic/abiotic processes taking place over the treatment period.

The results presented in Figure 19 suggest a redistribution of hydrocarbons between the soil and aqueous phases. Any redistribution, however, did not change the concentration of rTPH in the soil significantly, since there were approximately two orders of magnitude greater mass of rTPH in the soil than in the aqueous phase. A different sampling procedure was used on September 3. During this anomalous sample period, the water samples were drawn from the ports at a higher flow rate. It is believed that this resulted in significant volatilization of the contaminant from the sample. These results, except for the

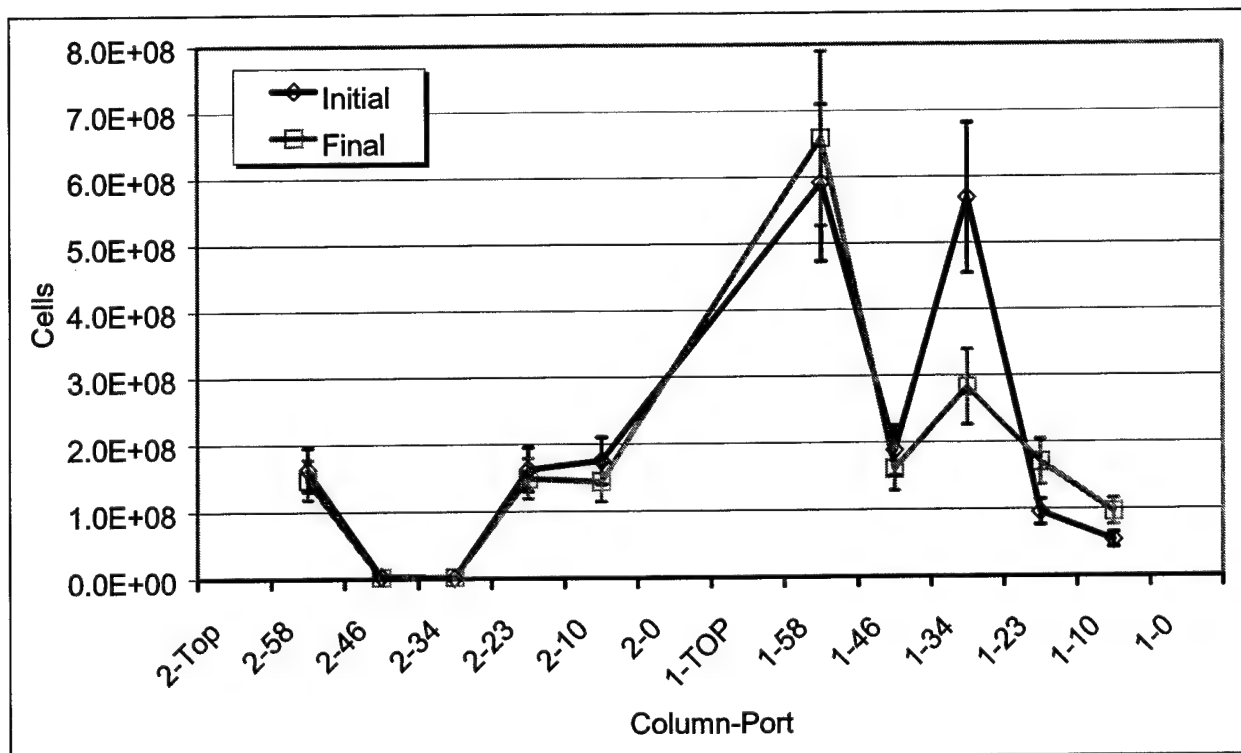


Figure 18. Biomass analysis of NA column at beginning and end of study

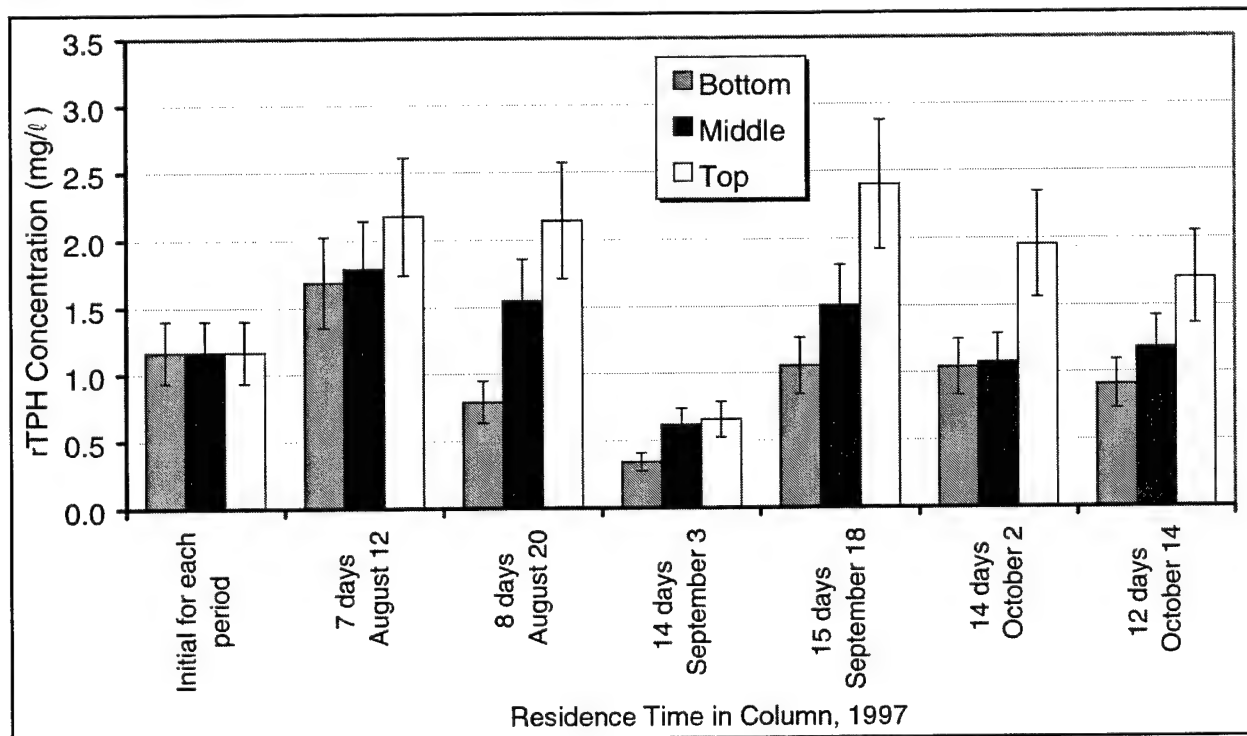


Figure 19. rTPH concentration in water – natural attenuation

Table 6
rTPH Concentration in Water – Natural Attenuation

Date, 1997	Residence Time, days	Aeration Rate, sccm	rTPH Concentration $\pm 20\%$ (mg/l)			
			Initial	Final Bottom	Final Middle	Final Top
Aug 12	7	0	1.16	1.69	1.78	2.17
Aug 20	8	0	1.16	0.790	1.55	2.14
Sep 3	14	0	1.16	0.339	0.616	0.658
Sep 18	15	0	1.16	1.05	1.50	2.40
Oct 2	14	0	1.16	1.04	1.07	1.95
Oct 14	12	0	1.16	0.910	1.18	1.71

anomalous results for samples taken on September 3, illustrated that natural attenuation processes in this core did not result in a significant decrease in the rTPH concentrations over a 10-week period.

Analysis of the removal rate of rTPH from the aqueous phase requires that the continuous exchange of the contaminant between the sorbed and aqueous phase be taken into account. Because no sorption studies were conducted for the contaminant and soil matrix in this study, the rate of rTPH desorption from the soil was estimated from changes in the aqueous rTPH concentrations in the upper saturated zone during the initial 7-day equilibration period. The rate of rTPH desorption was estimated using Equation 1. The first-order desorption-rate constant (k_{dr}) calculated for the natural attenuation column was 0.550 day^{-1} . The upper saturated zone was chosen because the soil in this area contained the highest level of rTPH contamination. Calculating the rate in this manner assumes no loss of rTPH from the aqueous phase during this time period. Undoubtedly, some level of rTPH was lost, either through volatilization or degradation during this time period. Therefore, the rate of desorption calculated is conservative. This rate of desorption is specific to this location and cannot be used at other locations in the contamination site. A partition coefficient and desorption rate constants for the contaminants of concern and soil type at a site should be developed from desorption studies for modeling purposes. The desorption rates calculated here, however, allow an aqueous-rTPH removal-rate constant to be calculated which can be used as an estimate for modeling contaminant transport at this site. Equation 1 is an example of a first-order desorption-rate constant and assuming that C_f at end of equilibration period is $0.99 \cdot C_e$:

$$\frac{dC}{dt} = k_{dr}(C_e - C)$$

$$k_{dr} = - \frac{\ln \left| \frac{\frac{C_f}{0.99} - C_f}{\frac{C_f}{0.99} - C_i} \right|}{t_f - t_i} \quad (1)$$

where

k_{dr} = first-order desorption-rate constant

C = TPH concentration in water

C_e = equilibrium TPH concentration in water

Using the desorption-rate constant calculated from the equilibrium period and the average change between the initial and final aqueous TPH concentration in the upper saturated zone, an average first-order removal-rate constant was calculated for the treatment periods following the equilibration period using Equation 2.

$$\frac{dC}{dt} = k_{dr}(C_e - C) - k_r C \quad (2)$$

where

K_r = first-order TPH removal-rate coefficient

$$\text{Assuming } \frac{dC}{dt} = 0 \rightarrow k_r = \frac{k_{dr}(C_e - C)}{C}$$

This calculation assumes that a steady aqueous-TPH concentration was reached by the end of each treatment period (i.e. the rate of desorption is equal to the rate of removal). The average removal-rate constant calculated, excluding the anomalous data point on September 3rd, was 0.04 day⁻¹.

Exit gas analysis. No gas was introduced into this column. Therefore, off gases could not be collected for analysis.

Bioventing

All data developed from the bioventing column is provided in Appendix C.

Soil phase rTPH and biomass concentrations. The bioventing evaluation was conducted by introducing air into the column above the saturated zone, through sampling port 1-34. Air was introduced to the column starting on day 7 after sampling the equilibration period. The results of initial and final measurements of soil rTPH and biomass from this column are shown in Figures 20 and 21, respectively. These results are from analyses conducted with large, 30-g soil samples collected from each port at the beginning of the experiment and at the completion of 9 weeks of bioventing, 10 weeks after the beginning of the experiment.

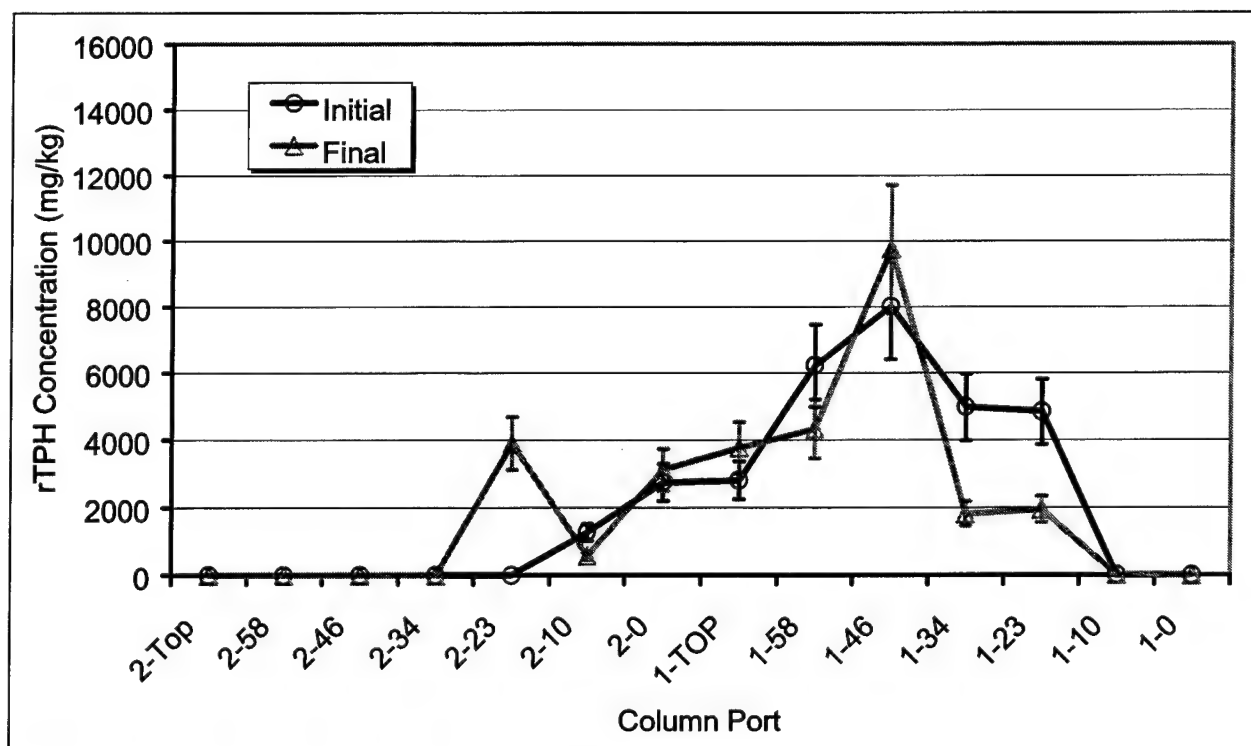


Figure 20. Initial and final soil rTPH concentrations – bioventing

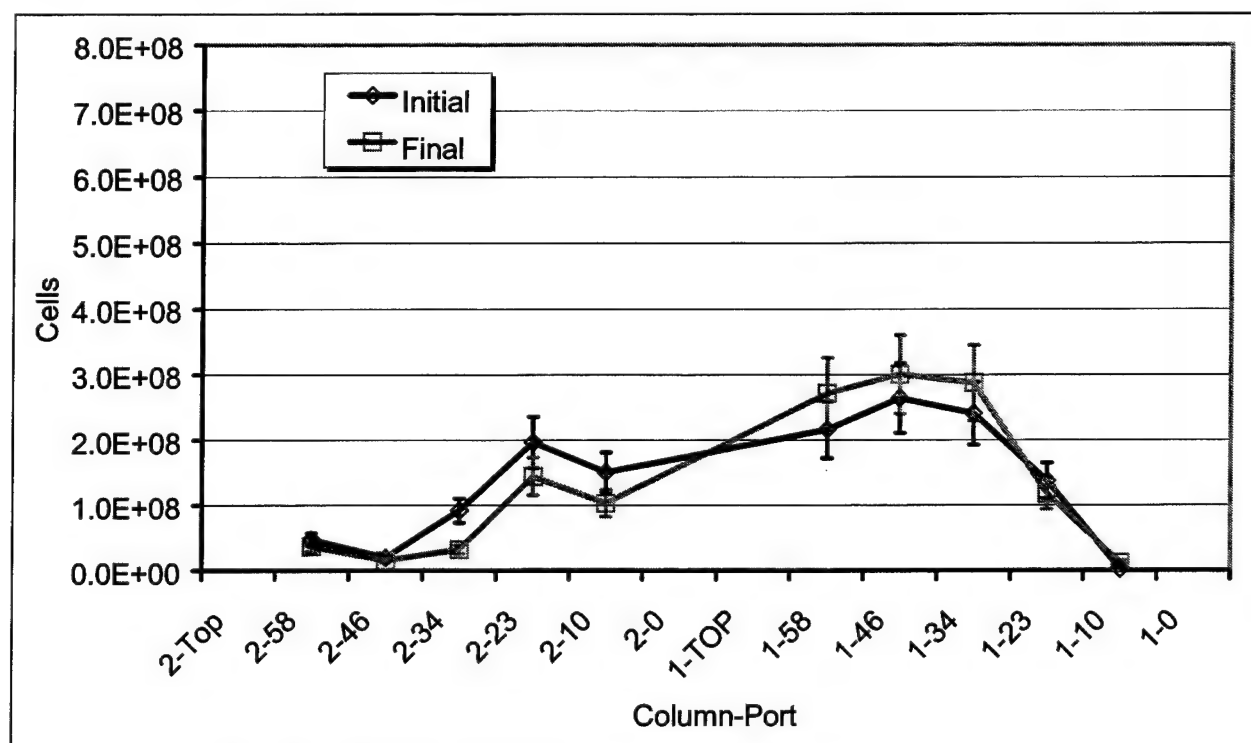


Figure 21. Initial and final biomass - bioventing

A mass balance of rTPH in the column showed the presence of 69.2 g ($\sigma = 13.8$) at the start of the experiment and 63.1 g ($\sigma = 12.6$) at the end. No significant change in the TPH concentration was observed during the 9-week treatment period as a result of bioventing the column.

Similarly, the biomass data presented in Figure 21 also show no significant change in the biomass concentration as a result of introducing air in the vadose zone.

Aqueous phase rTPH concentrations. Total petroleum concentration in water samples from the bottom, middle, and top of the saturated zone are illustrated in Figure 22 for each treatment period and listed in Table 7. As identified earlier, the saturated zone was drained at the end of each sampling period as described in the paragraph "Water sampling method" of Phase II, Chapter 2. Contaminated groundwater from the site was then added to the column. This water sampling method simulated the movement of groundwater through a specified aquifer zone and avoided cross contamination between the various column levels during water sampling. Any change in the aqueous contaminant concentration during a treatment period is the cumulative result of interactions between groundwater and contaminated soil, and of any biotic/abiotic processes taking place over the treatment period.

The results presented in Figure 22 indicate that the rTPH concentration of water in the top of the saturated zone increased by a factor 7 (approximately) during the equilibration period. rTPH concentrations in water from the middle and bottom of the saturated zone did not change significantly during the equilibration period indicating much lower levels of soil contamination. These data suggest a redistribution of hydrocarbons between the soil and aqueous phases. Any redistribution, however, did not change the concentration of rTPH in the soil significantly, as there were approximately two orders of magnitude greater mass of rTPH in the soil as there were in the aqueous phase.

An analysis of the aqueous rTPH concentrations was conducted as described in the paragraph, "Aqueous phase rTPH concentrations," Phase II, Chapter 2. Using Equation 1, a desorption-rate constant of 0.635 day^{-1} in the upper saturated zone was determined. Using the desorption-rate constant and Equation 2, a removal-rate constant of 2.07 day^{-1} was found for the upper saturated zone. As with the natural-attenuation column, the anomalous data point of September 3 was not used in the analysis.

Exit gas analysis. Air was initially introduced to the column at a flow rate of 4 sccm. After 5 weeks, the flow rate of air into the column was reduced to 1 sccm. An air flow rate of 1 sccm corresponds to an estimated specific flow rate of 49-sccm air/kg soil/day, an average linear velocity of approximately 5.6 cm/hr, and an estimated residence time of 60 hr in the soil.

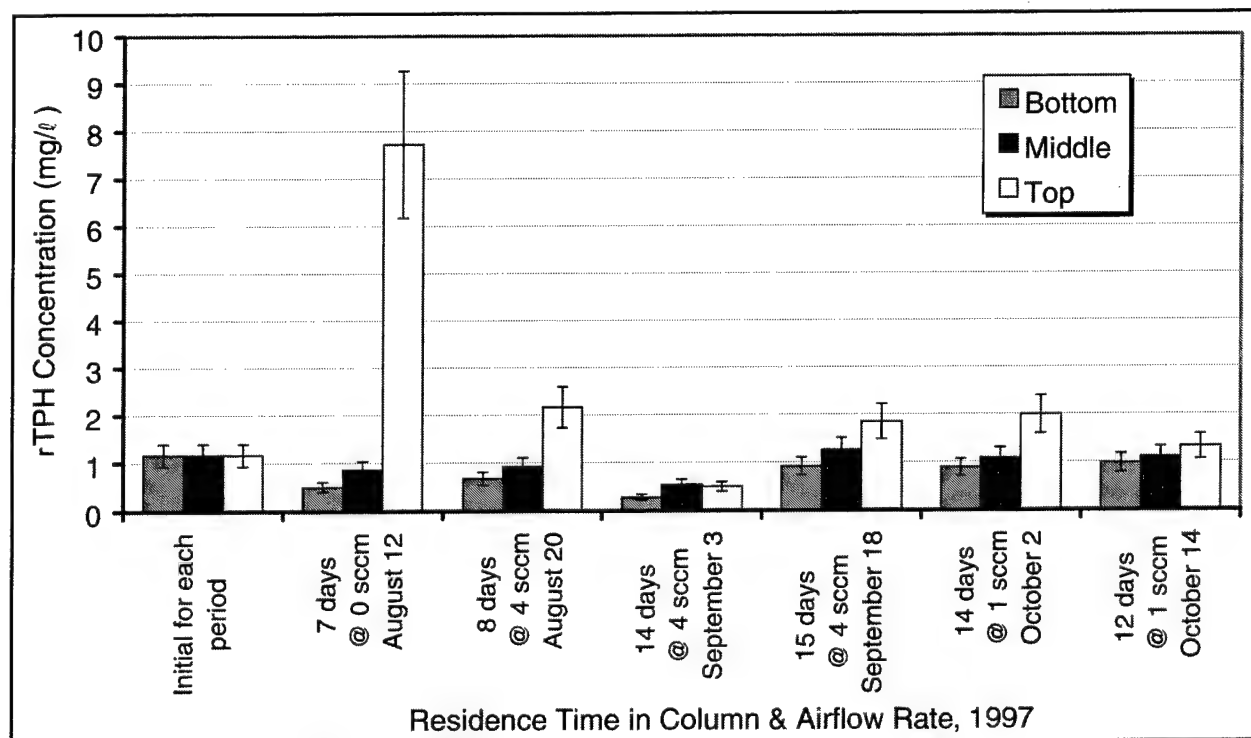


Figure 22. rTPH concentration in water - bioventing

Table 7						
rTPH Concentrations in Water – Bioventing						
Date, 1997	Residence Time, days	Aeration Rate, sccm	rTPH Concentration \pm 20% (mg/l)			
			Initial	Final Bottom	Final Middle	Final Top
Aug 12	7	0	1.16	0.502	0.861	7.72
Aug 20	8	4	1.16	0.675	0.920	2.16
Sep 3	14	4	1.16	0.278	0.537	0.494
Sep 18	15	4	1.16	0.915	1.25	1.84
Oct 2	14	1	1.16	0.885	1.08	1.99
Oct 14	12	1	1.16	0.975	1.10	1.32

The analysis of oxygen and carbon dioxide in the exit gas showed signs of significant biological activity in the column. As air was passed through the column, the volume fraction of oxygen decreased while the volume fraction of carbon dioxide increased. The measured volume fractions of oxygen and carbon dioxide in the inlet and exit gases passing through the bioventing column are presented in Figure 23. These respiration data are clearly indicative of biological activity in the column.

The cumulative consumption of oxygen and production of carbon dioxide were calculated from airflow rates and of compositions of inlet and exit gases. Calculations of oxygen consumption and CO₂ production were based on Equations 3 and 4, respectively.

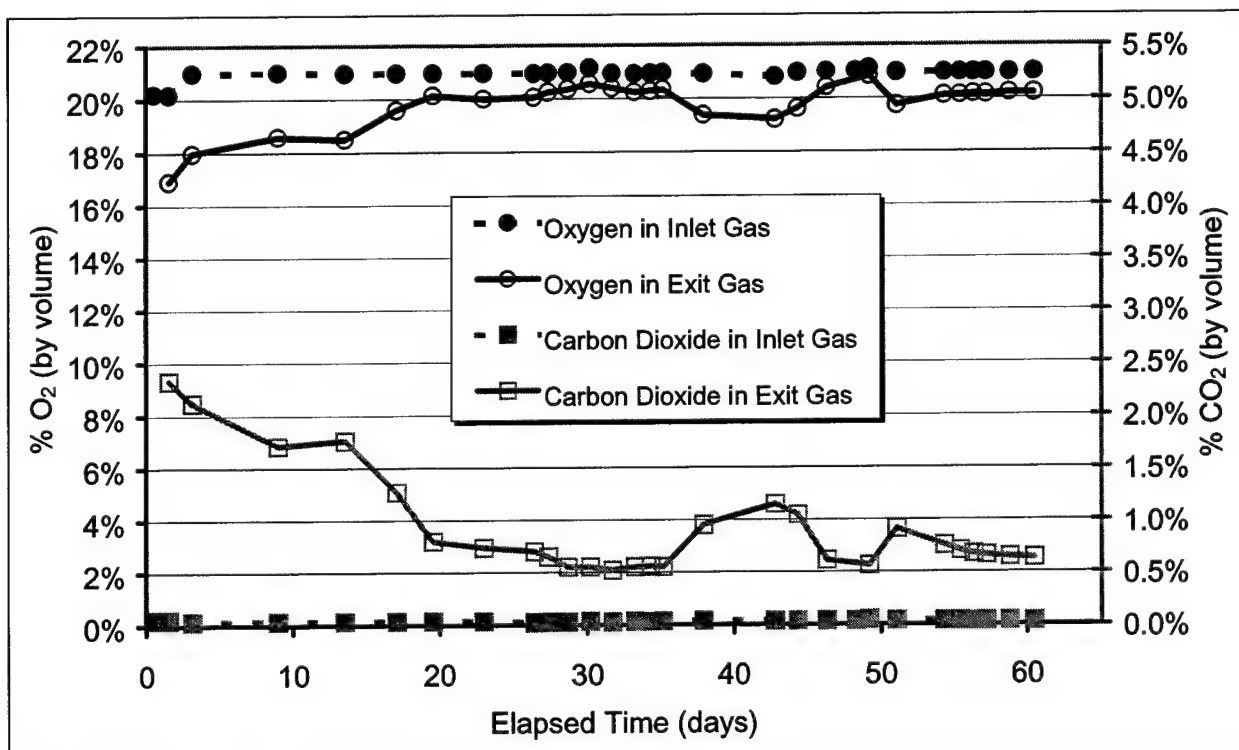


Figure 23. Inlet and outlet O₂ and CO₂ concentrations - bioventing

$$\Delta O_2 = \frac{Q}{22,400} \left[O_2^{in} - O_2^{out} \left(\frac{1 - O_2^{in} - CO_2^{in}}{1 - O_2^{out} - CO_2^{out}} \right) \right] \Delta t \cdot 1,440 \quad (3)$$

where

Q = airflow rate in standard cubic centimeters per minute

Δt = elapsed time in days

O_2 = mole fraction of oxygen

CO_2 = mole fraction of carbon dioxide

$$\Delta CO_2 = \frac{Q}{22,400} \left[CO_2^{out} - CO_2^{in} \left(\frac{1 - O_2^{in} - CO_2^{in}}{1 - O_2^{out} - CO_2^{out}} \right) \right] \Delta t \cdot 1,440 \quad (4)$$

where

Q = airflow rate in standard cubic centimeters per minute

Δt = elapsed time in days

O_2 = mole fraction of oxygen

CO_2 = mole fraction of carbon dioxide

$$\frac{22,400 \text{ standard cm}^3}{\text{mole}} \quad \frac{1,440 \text{ min}}{\text{day}}$$

The cumulative oxygen consumption and carbon dioxide production data are shown in Figure 24. Since there is a well defined relationship between aerobic hydrocarbon metabolism and oxygen consumption of 3.2 g oxygen per gram hydrocarbon,¹ the data in Figure 24 can be converted into cumulative biodegradation of rTPH. Over the 9 weeks of bioventing, the total mass of contaminant degraded calculated from oxygen consumption data is 1.77 g. Looking at Figure 24, a steady rate of oxygen consumption and carbon dioxide production was reached and can be seen from day 42 to day 62. From these data, a steady oxygen consumption rate of 0.57 ($\sigma = 0.02$) mmole/day and a steady carbon dioxide production rate of 0.45 ($\sigma = 0.01$) mmole/day were calculated. The estimated mass of contaminated soil in the column was 17.3 kg. The corresponding zero-order rate of hydrocarbon biological degradation from day 42 to day 62 was therefore 0.33-mg hydrocarbon kg contaminated soil⁻¹ day⁻¹. Additionally, a comparison of exit gas data under two different rates of bioventing suggested little benefit from blowing air at a higher rate than the guidance given in the EPA Manual.² The oxygen levels in the exit gases were at the same level under both aeration rates.

The ratio of the carbon dioxide production rate and oxygen consumption rate is known as the respiration quotient (RQ). The characteristic value of RQ is dependent upon the nature of the substrate being metabolized by the cells. When carbohydrates are the substrate of interest, RQ values around 1.0 are generally observed under aerated conditions. Under the same conditions, metabolism of hydrocarbons yields RQ values around 0.67. For the bioventing column, an RQ value of 0.78 was observed suggesting hydrocarbon metabolism.

The difference between contaminant present in the soil column, ~56 g rTPH, and the calculated total mass of contaminant biologically degraded, 1.77 g rTPH, is large. In this context, the absence of a statistically significant decrease in contaminant mass within the column is not surprising. More directly, the observed lack of any statistically significant decrease in rTPH in the bioventing

¹ J. T. Cookson, Jr. (1995). *Bioremediation engineering – Design and application*. McGraw-Hill, New York.

² USEPA. (1995). Op. cit.

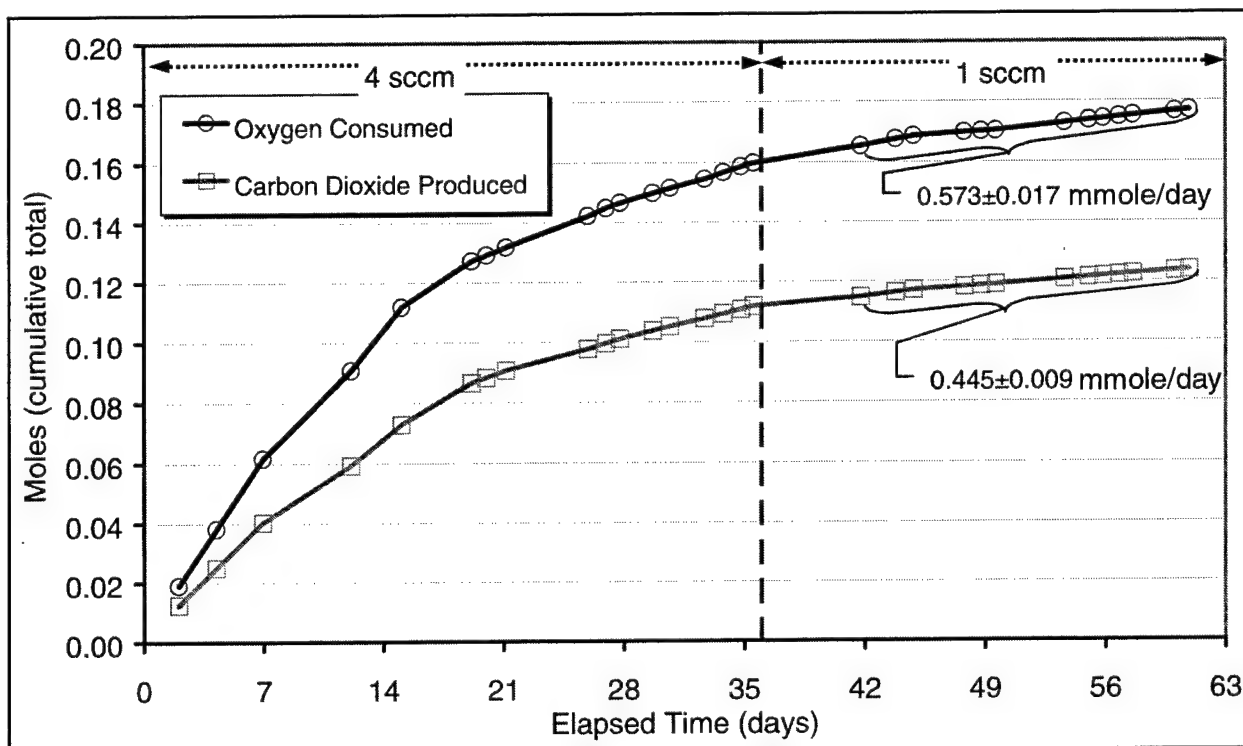


Figure 24. Cumulative O₂ consumption and CO₂ production vs time – bioventing

column does not indicate a lack of biological activity; it only suggests that the change is not statistically significant. By contrast, the exit gas analysis and corresponding RQ values clearly indicate biological degradation activity in the column. This information suggests that the duration of the study was not sufficient for the level of contamination in the soil.

Biosparging

All data developed from the biosparging column are provided in Appendix D.

Soil phase TPH and biomass concentrations. The biosparging evaluation was conducted by introducing air through the bottom plug of the column, port 1-0. Airflow was initiated starting on day 7, after the equilibration period. The results of initial and final measurements of soil rTPH and biomass measurements from this column are shown in Figures 25 and 26, respectively. These results are from analyses conducted with large, 30-g, soil samples collected from each port at the beginning of the experiment and at the completion of 9 weeks of biosparging, 10 weeks after the beginning of the experiment.

A mass balance of rTPH in the column showed the presence of 75.9 g ($\sigma = 15.2$) at the start of the experiment and 39.3 g ($\sigma = 7.9$) at the end. It can be said with 98 percent confidence that there was a decrease of total rTPH in the column over the duration of the evaluation. Biosparging appears to have resulted in a reduction of rTPH in the column of 36.6 g with a 95 percent confidence interval

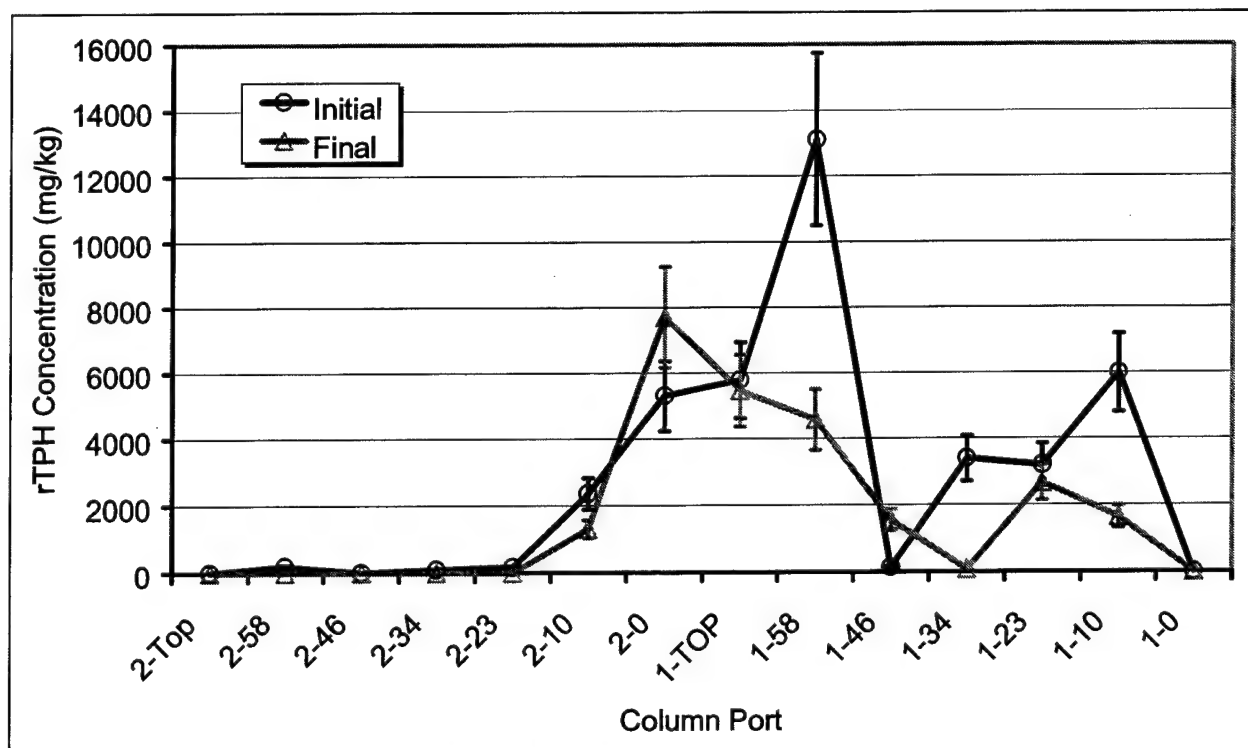


Figure 25. Initial and final soil rTPH concentration – biosparging

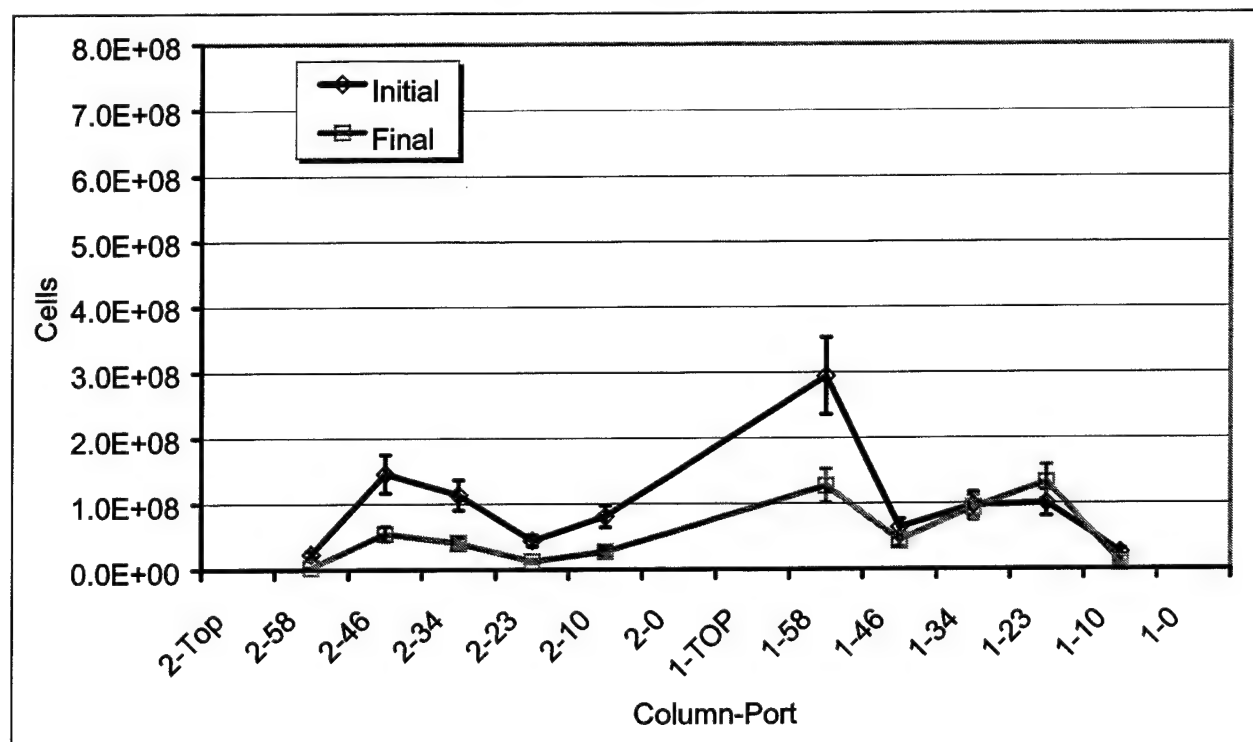


Figure 26. Initial and final biomass – biosparging

from 8.4 to 64.8. Analyses of 1-g soil samples from intermediate time points show a large deviation of rTPH in the column and trend was discernible.

A total removal rate of TPH from the column was calculated using the initial and final rTPH levels in the column. The zero-order (concentration independent) rate was calculated to be 35.5-mg rTPH/kg contaminated soil/day. This removal rate is based on the estimated mass of contaminated soil in the column. A gross estimate of the time required for removal of the contamination can be achieved by dividing the highest concentration of TPH in the soil by this rate.

Microbial mass in the column (Figure 26) showed a significant reduction in most areas of the column. The reduction of viable biomass could be the result of changing the environment in the soil from anoxic, to which the majority of the biomass was acclimated, to aerobic conditions.

Aqueous Phase rTPH Concentrations. Total petroleum concentration in water samples from the bottom, middle, and top of the saturated zone are illustrated in Figure 27 for each treatment period and listed in Table 8. During the initial 7-day equilibration period, no air was forced into the soil column. As in the bioventing column, the rTPH concentration of water in the top of the saturated zone increased by a factor of approximately 7 during this period. rTPH concentrations in water from the middle and bottom of the saturated zone did not change significantly during the equilibration period, thus indicating much lower levels of soil contamination.

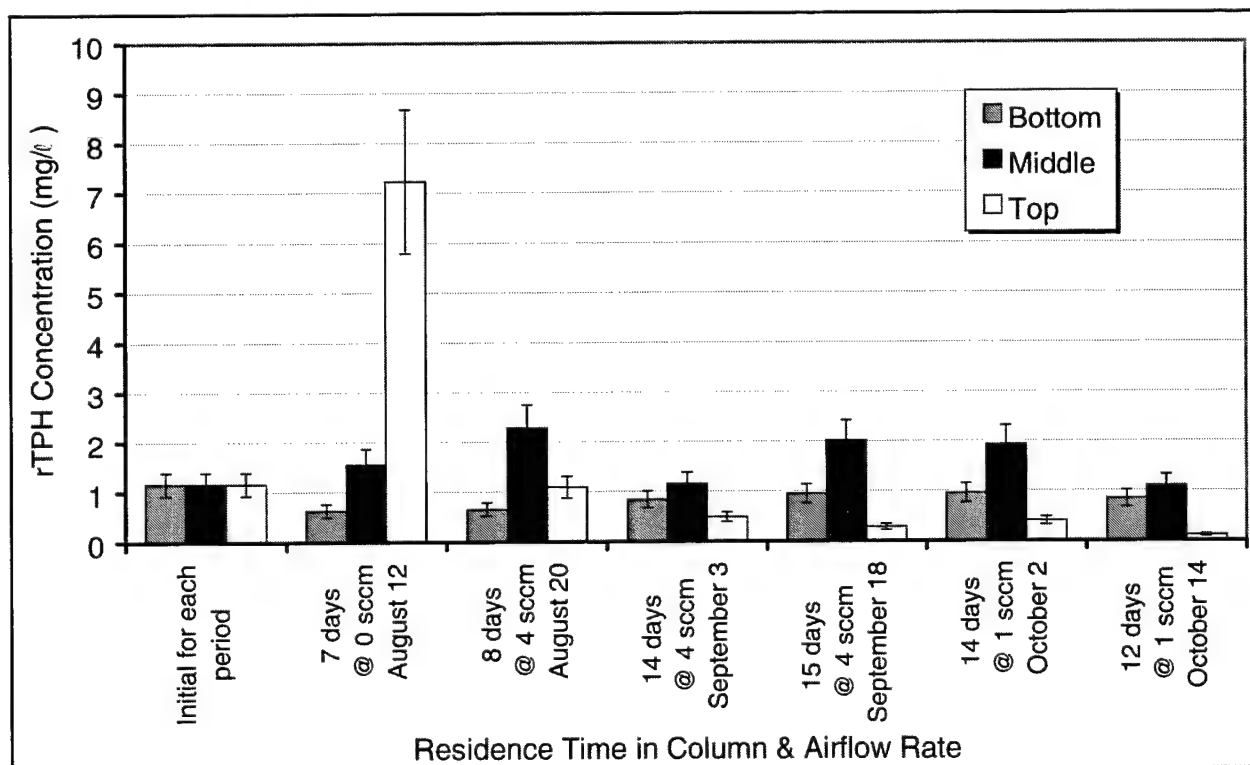


Figure 27. rTPH concentration in water – biosparging

Table 8
rTPH Concentrations in Water – Biosparging

Date, 1997	Residence Time, days	Aeration Rate, sccm	rTPH Concentration \pm 20%, mg/l			
			Initial	Final Bottom	Final Middle	Final Top
Aug 12	7	0	1.17	0.633	1.55	7.23
Aug 20	8	4	1.17	0.655	2.29	1.09
Sep 3	14	4	1.17	0.843	1.16	0.489
Sep 18	15	4	1.17	0.951	2.01	0.284
Oct 2	14	1	1.17	0.961	1.93	0.405
Oct 14	12	1	1.17	0.844	1.10	0.107

At sample events following the equilibration period, the aqueous phase contaminant concentrations at the top of the saturated zone decreased dramatically. This reduction of contaminants in the aqueous phase, or rather the lack of increase, indicates a rate of aqueous phase contaminant degradation exceeding the rate of contaminant desorption from the soil. A similar reduction in aqueous contaminant concentrations was not observed in the middle and lower levels of the saturated zone. This is possibly the result of a lower overall population of viable biomass in these zones. It is believed that biological degradation and not volatilization is the most significant path of rTPH removal from the aqueous phase. If volatilization were the major path for rTPH removal in the aqueous phase, much larger reductions of rTPH concentrations should have been observed in the middle and lower levels of the saturated zone.

An analysis of the aqueous rTPH concentrations was conducted as described in the paragraph "Aqueous phase rTPH concentrations," Phase II, Chapter 2. Using Equation 1, a desorption-rate constant of 0.633 day^{-1} in the upper saturated zone was determined. Using the desorption-rate constant and Equation 2, a removal rate constant of 9.16 day^{-1} was found for the upper saturated zone. As with the natural-attenuation and bioventing columns, the anomalous data point of September 3 was not used in the analysis.

Exit Gas Analysis. Air was initially introduced to the column at a flow rate of 4 sccm. After 5 weeks, the flow rate of air into the column was reduced to 1 sccm. An air flow rate of 1 sccm corresponds to an estimated specific flow rate of 50-scc air/kg soil/day, an average linear velocity of approximately 5.6 cm/hr, and an estimated residence time of 58 hr in the soil.

The analysis of oxygen and carbon dioxide in the exit gas of the biosparging column showed signs of significant biological activity in the column. As air was passed through the column, the volume fraction of oxygen decreased while the volume fraction of carbon dioxide increased. The measured volume fractions of oxygen and carbon dioxide in the inlet and exit gases are presented in Figure 28. These respiration data are clearly indicative of biological activity in the column.

The cumulative consumption of oxygen and production of carbon dioxide were calculated from airflow rates and of compositions of inlet and exit gases. Calculations of oxygen consumption and CO_2 production were based on

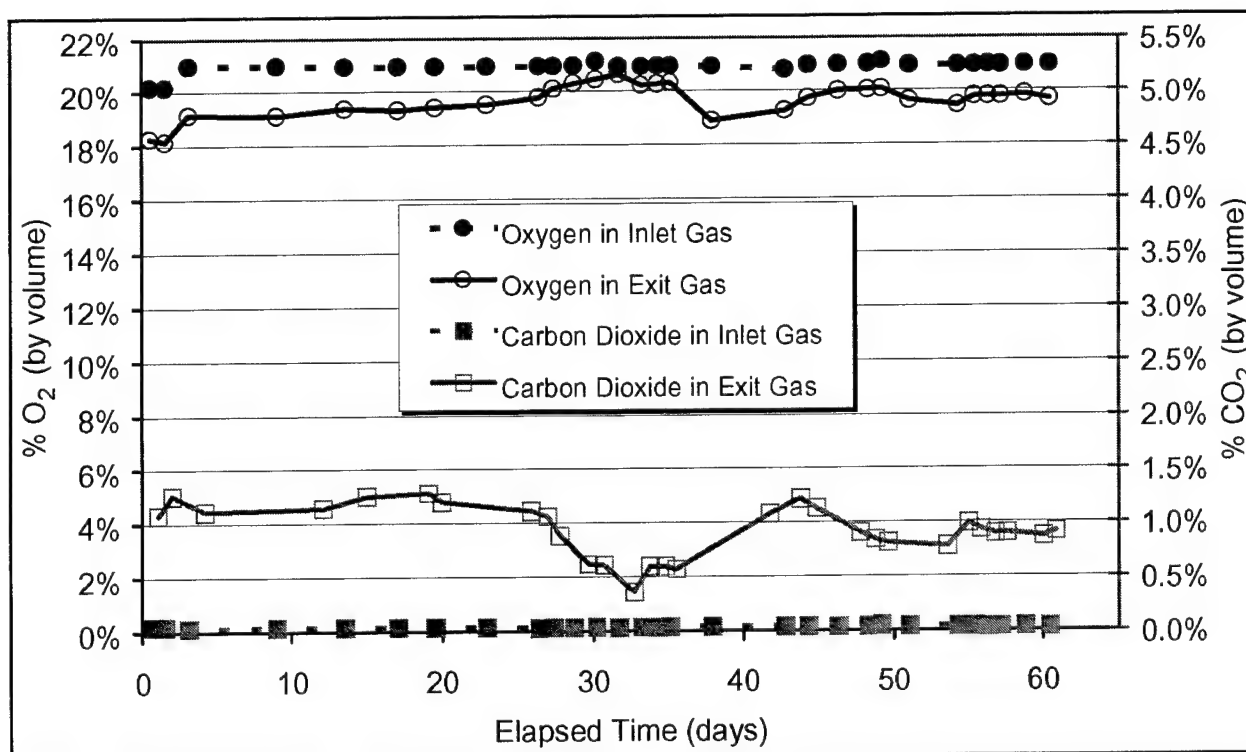


Figure 28. Inlet and outlet O₂ and CO₂ concentrations – biosparging

Equations 3 and 4, respectively. The cumulative oxygen consumption and carbon dioxide production data are shown in Figure 29. As was done for the bioventing column, the data in Figure 29 can be converted into cumulative biodegradation of TPH. Over the 9 weeks of biosparging, the total mass of contaminant degraded calculated from oxygen consumption data is 1.60 g. Looking at Figure 29, a steady rate of oxygen consumption and carbon dioxide production was reached and can be seen from day 42 to 62. From these data, a steady oxygen consumption rate of 0.80 ($\sigma = 0.01$) mmole/day and a steady carbon dioxide production rate of 0.54 ($\sigma = 0.01$) mmole/day was calculated. The estimated mass of contaminated soil in the column was 16.4 kg. The corresponding rate of hydrocarbon biological degradation was therefore 0.49-mg hydrocarbon kg contaminated soil⁻¹ day⁻¹. Additionally, a comparison of exit gas data under two different rates of bioventing suggested little benefit from blowing air at a higher rate than the guidance given in the EPA Manual.¹ The oxygen levels in the exit gases were at the same level under both aeration rates.

As explained in the paragraph "Exit gas analysis," Phase II, Chapter 2, the characteristic RQ value for hydrocarbon metabolism is around 0.67. The RQ value for the biosparging column was observed to be 0.68, which strongly suggests hydrocarbon metabolism.

¹ Ibid.

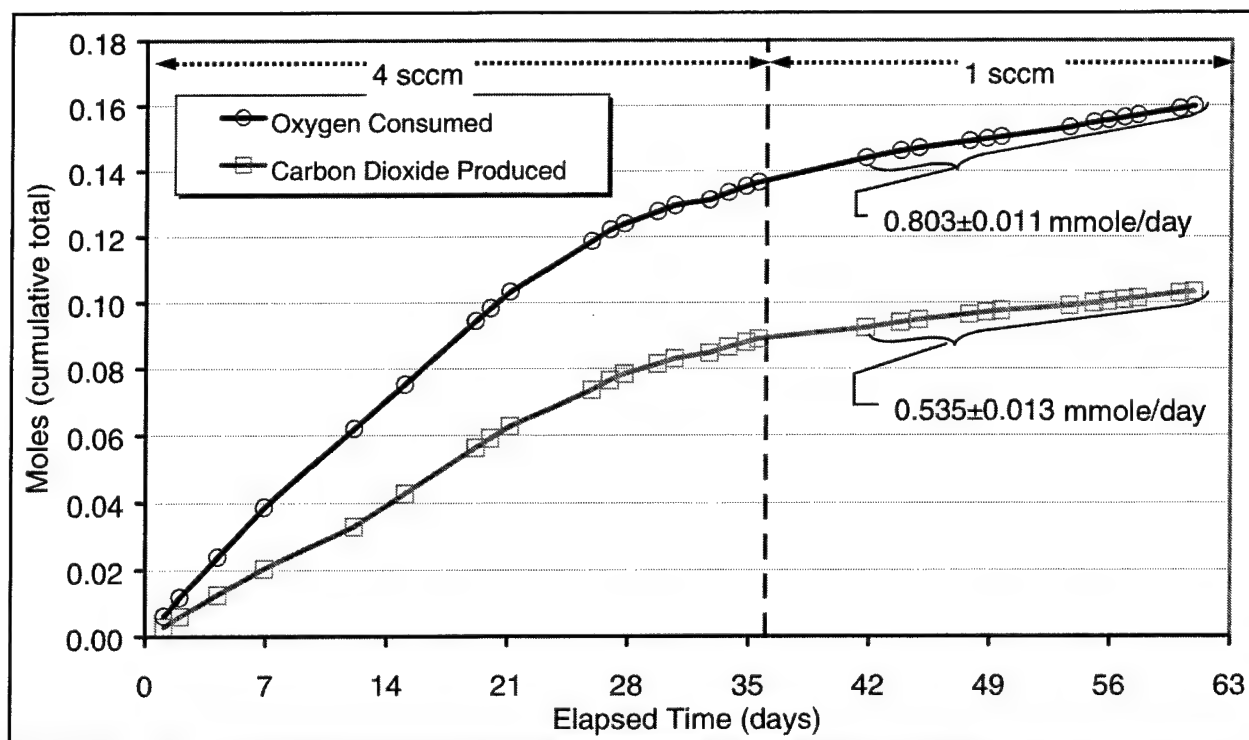


Figure 29. Cumulative O₂ consumption and CO₂ production vs time – biosparging

Conclusions from Phase II

The rates of biodegradation in the cases of bioventing and biosparging were calculated from the exit gas analyses. These resulted in steady state biodegradation rates of 0.33- and 0.49-mg rTPH kg contaminated soil⁻¹ day⁻¹ for bioventing and biosparging, respectively. These data suggest that the total estimated time to biologically degrade the contaminant under biosparging and bioventing scenarios will be comparable. The biodegradation rates listed above include no physical means of rTPH removal or incorporation of the contaminant in biomass. The biodegradation rates are therefore conservative estimates of rate of rTPH removal from the soil.

As a result of the high level of contamination in the columns and duration of the study, 10 weeks, a total removal rate of rTPH from the soil columns could be calculated. Based on the rTPH balances, no biodegradation activity was evident in the natural attenuation column. This does not indicate that there was no biodegradation under natural attenuation. It simply reflects the fact that the duration of the evaluation was not sufficient to discern any change in total rTPH concentrations in this column.

Based on the analysis of soil and aqueous phases, rTPH in this system was present predominantly in the soil phase. However, the major mode of transport, and often the area of most concern in the environment, is the aqueous phase of the contaminant. Analysis of the aqueous rTPH concentrations in the top of the saturated zone indicated first-order removal-rate constants of 2.07, 9.16, and 0.04 day⁻¹ for the bioventing, biosparging, and natural attenuation columns,

respectively. Comparison of these removal rates indicates that the level of biological activity was much slower in the natural attenuation column than in both the bioventing and biosparging columns. While both bioventing and biosparging showed considerable removal of rTPH from the aqueous phase (compared to equilibrated concentrations), the removal rate from in the biosparging was much higher. This suggests that biosparging will be a more effective method of attenuating migration of rTPH in the groundwater.

Appendix A

Phase I Data

Initial Soil Analyses using PLFA – Raw Data											
Sample	Depth (ft)	pmole/g	Mole %						Ratio		
		PLFA ¹	nsat ²	terbrsat ³	mono ⁴	brmono ⁵	mibrsat ⁶	poly ⁷	n16/c ⁸	n18/c ⁹	i15/a15 ¹⁰
A0a	0.0	14787	14.99	14.72	49.95	3.60	13.75	2.98	0.08	0.0	2.34
A0sd	0.0	4654	0.16	1.82	2.91	0.22	1.15	0.27	0.01	0.0	0.14
A2.5a	2.5	422	27.06	21.98	34.65	0.00	6.08	10.23	0.00	0.0	0.00
A2.5sd	2.5	255	11.75	16.40	4.39	0.00	2.51	4.55	0.00	0.0	0.00
A5a	5.0	1749	14.54	18.72	55.00	2.61	6.62	2.51	0.00	0.0	0.90
A5sd	5.0	134	1.43	0.71	1.38	0.03	0.46	0.56	0.00	0.0	0.05
5'2"	5.2	7676	8.4	9.1	81.5	0.8	0.3	0.0	0.1	0.1	6.2
5'4"	5.3	5955	7.9	5.9	84.9	1.3	0.0	0.0	0.2	0.1	6.7
5'6"	5.5	9938	7.5	10.1	80.3	2.1	0.0	0.0	0.1	0.1	6.4
5'8"	5.7	5233	6.8	8.4	83.3	1.5	0.0	0.0	0.1	0.1	4.4
5'10"	5.8	9575	7.3	13.4	75.1	1.3	2.8	0.0	0.0	0.1	2.3
6'	6.0	4662	7.5	15.0	76.5	0.5	0.4	0.0	0.0	0.0	2.0
6'2"	6.2	3254	7.2	7.7	82.4	0.6	2.1	0.0	0.0	0.0	1.4
6'4"	6.3	2872	9.1	6.1	83.7	0.0	1.1	0.0	0.2	0.0	0.9
6'6"	6.5	4213	18.3	9.2	56.9	2.1	11.9	1.7	0.0	0.1	1.4
A7.5a	7.5	5878	14.19	11.59	68.95	4.82	0.00	0.45	0.27	0.07	2.72
A7.5sd	7.5	2053	5.30	1.50	12.49	5.37	0.00	0.61	0.02	0.00	1.69
7'8"	7.7	5903	14.7	7.6	76.9	0.8	0.0	0.0	0.2	0.1	3.7
7'10"	7.8	3432	6.6	4.5	88.3	0.6	0.0	0.0	0.2	0.1	5.8
8'	8.0	9053	9.1	9.5	79.2	2.3	0.0	0.0	0.2	0.1	3.7
8'2"	8.2	5098	9.6	8.1	81.1	1.2	0.0	0.0	0.1	0.1	3.9
A8.5a	8.5	3874	10.02	8.30	80.28	1.22	0.19	0.0	0.19	0.13	2.92
A8.5sd	8.5	422	0.35	1.98	2.45	0.46	0.32	0.0	0.01	0.01	0.15
8'8"	8.7	6530	9.2	5.3	84.9	0.6	0.0	0.0	0.1	0.2	4.7
8'10"	8.8	6148	9.2	4.0	86.8	0.0	0.0	0.0	0.1	0.2	4.3
9'	9.0	5040	9.0	4.1	86.8	0.0	0.0	0.0	0.1	0.3	3.9
10'2"	10.2	5083	16.2	14.1	66.3	1.1	2.3	0.0	0.1	0.0	1.5
A10.5a	10.5	11854	17.62	11.20	51.10	2.34	8.26	9.47	0.10	0.03	1.92
A10.5sd	10.5	2835	0.09	2.68	0.74	0.17	0.21	3.59	0.01	0.00	0.08
A11.5a	11.5	6800	16.03	6.49	75.28	0.77	0.54	0.88	0.10	0.16	1.96
A11.5sd	11.5	2074	1.07	1.97	3.12	0.23	0.02	0.03	0.00	0.01	0.16
12'	12.0	20272	14.8	4.1	80.1	0.5	0.1	0.2	0.1	0.2	1.9
12'2"	12.2	16087	16.3	4.6	78.7	0.3	0.0	0.2	0.1	0.1	2.4
12'4"	12.3	13547	20.8	2.1	77.0	0.2	0.0	0.0	0.1	0.1	2.4
12'6"	12.5	16670	18.3	1.2	80.1	0.4	0.0	0.0	0.1	0.1	2.5
12'8"	12.7	12792	24.6	2.9	72.0	0.3	0.0	0.3	0.0	0.1	1.4
12'10"	12.8	8179	25.9	7.0	67.1	0.0	0.0	0.0	0.1	0.1	1.3
13'	13.0	5633	24.2	3.5	72.4	0.0	0.0	0.0	0.1	0.1	1.1
13'2"	13.2	8062	22.6	7.3	69.8	0.0	0.3	0.0	0.1	0.1	1.2
A13.5a	13.5	2542	19.02	7.71	71.21	1.31	0.58	0.16	0.10	0.13	1.76
A13.5sd	13.5	349	0.73	2.22	2.63	0.47	0.51	0.28	0.01	0.01	0.12
A15a	15.0	688	27.96	13.33	56.08	0.00	0.82	1.82	0.13	0.00	2.32
A15sd	15.0	82	4.53	7.99	4.52	0.00	0.95	2.22	0.01	0.00	0.95

Bold indicates replicate analyses (n=3)
¹ ester-linked phospholipid fatty acids
² normal saturates
³ terminally branched saturates
⁴ monounsaturates
⁵ branched monounsaturates
⁶ mid-chain branched saturates
⁷ polyunsaturates
⁸ 16:1w7/16:1w7c
⁹ 18:1w7/18:1w7c
¹⁰ iso15:0/anteiso15:0

Sheet 1 of 3

Initial Soil Analyses using PLFA – Raw Data (Continued)														
Sample	Depth (ft)	Normal Saturates					Terminally branched saturates					Monounsaturates		
		15:0	16:0	17:0	18:0	20:0	i14:0	i15:0	a15:0	i16:0	i17:0	a17:0	16:1w9c	16:1w7c
A0a	0.0	0.43	11.04	0.91	2.62	0.00	0.32	4.42	1.66	4.11	1.94	2.05	1.57	5.90
A0sd	0.0	0.04	0.47	0.52	0.08	0.00	0.19	0.92	0.29	0.34	0.17	0.21	0.18	1.17
A2.5a	2.5	0.00	15.23	1.60	10.23	0.00	5.88	2.45	2.84	4.08	1.32	5.41	0.00	1.94
A2.5sd	2.5	0.00	4.15	2.77	4.92	0.00	5.09	2.12	2.47	3.53	1.16	2.06	0.00	1.68
A5a	5.0	0.00	10.06	1.16	3.32	0.00	1.19	3.33	3.70	4.61	2.86	3.03	2.02	6.73
A5sd	5.0	0.00	0.86	0.44	0.14	0.00	1.08	0.42	0.28	0.17	0.21	0.36	0.10	0.35
5'2"	5.2	0.4	7.2	0.3	0.4	0.0	0.3	4.8	0.8	2.6	0.5	0.0	1.7	4.2
5'4"	5.3	0.0	7.2	0.3	0.4	0.0	0.0	2.8	0.4	2.3	0.3	0.0	0.9	3.6
5'6"	5.5	0.1	6.6	0.2	0.5	0.0	0.1	4.0	0.6	4.7	0.4	0.2	1.6	3.0
5'8"	5.7	0.0	6.4	0.0	0.4	0.0	0.2	2.6	0.6	4.7	0.2	0.0	1.2	2.5
5'10"	5.8	0.5	5.6	0.0	1.3	0.0	0.6	4.1	1.8	5.7	0.6	0.6	1.9	3.1
6'	6.0	0.0	6.5	0.0	1.1	0.0	0.4	3.8	1.9	8.0	0.4	0.6	2.2	3.0
6'2"	6.2	0.0	5.7	0.0	1.5	0.0	0.0	1.1	0.8	6.2	0.0	0.7	1.4	2.7
6'4"	6.3	0.0	8.0	0.0	1.1	0.0	0.0	1.2	1.3	3.7	0.0	0.0	1.6	2.8
6'6"	6.5	0.0	14.2	0.0	3.6	0.5	0.0	1.6	1.2	2.3	2.1	2.1	0.9	5.5
A7.5a	7.5	0.39	6.55	4.94	1.35	0.96	0.86	3.65	2.02	3.02	1.35	0.69	1.73	3.41
A7.5sd	7.5	0.07	0.49	6.15	0.14	0.34	0.41	0.58	1.70	0.32	0.05	0.19	0.12	0.20
7'8"	7.7	0.7	11.9	0.3	1.8	0.0	0.3	3.4	0.9	2.1	0.5	0.3	1.2	3.6
7'10"	7.8	0.0	6.1	0.0	0.5	0.0	0.0	2.2	0.4	1.4	0.6	0.0	0.9	2.4
8'	8.0	0.7	6.9	0.5	1.0	0.0	0.5	3.8	1.0	2.6	1.3	0.4	2.0	3.8
8'2"	8.2	0.4	7.9	0.4	1.0	0.0	0.4	3.3	0.9	2.0	1.3	0.2	1.9	4.0
A8.5a	8.5	0.25	6.83	0.93	2.01	0.00	0.94	2.26	0.77	1.63	1.89	0.87	1.55	3.43
A8.5sd	8.5	0.06	0.13	0.23	0.12	0.00	0.62	0.79	0.25	0.22	0.11	0.12	0.28	0.35
8'8"	8.7	0.2	7.6	0.3	1.0	0.0	0.2	2.1	0.5	0.8	1.8	0.0	1.6	4.8
8'10"	8.8	0.0	7.6	0.2	1.4	0.0	0.0	1.5	0.3	0.6	1.6	0.0	1.4	4.1
9'	9.0	0.0	7.3	0.3	1.4	0.0	0.0	1.3	0.3	0.7	1.8	0.0	1.3	4.1
10'2"	10.2	0.6	14.1	0.3	1.3	0.0	0.5	4.0	2.7	4.4	1.7	0.8	1.5	8.4
A10.5a	10.5	0.45	13.05	0.82	2.98	0.33	0.41	2.79	1.47	3.08	1.39	2.06	1.02	7.34
A10.5sd	10.5	0.13	0.21	0.07	0.26	0.04	0.27	1.13	0.63	0.52	0.04	0.10	0.19	1.58
A11.5a	11.5	0.17	13.08	0.92	1.86	0.00	0.58	1.46	0.77	1.15	1.79	0.75	1.08	8.52
A11.5sd	11.5	0.02	1.08	0.15	0.21	0.00	0.50	0.69	0.40	0.21	0.09	0.09	0.29	1.79
12'	12.0	0.4	13.9	0.5	0.0	0.0	0.1	1.4	0.8	0.6	1.2	0.1	1.3	10.5
12'2"	12.2	0.4	14.6	0.6	0.8	0.0	0.1	2.0	0.8	0.8	0.7	0.2	1.2	13.7
12'4"	12.3	0.2	19.5	0.6	0.5	0.0	0.0	0.8	0.4	0.3	0.4	0.1	0.7	16.7
12'6"	12.5	0.1	17.4	0.3	0.5	0.0	0.0	0.5	0.2	0.1	0.4	0.0	0.4	16.9
12'8"	12.7	0.3	23.2	0.5	0.5	0.0	0.0	1.1	0.8	0.3	0.5	0.1	0.4	23.8
12'10"	12.8	0.6	23.9	0.8	0.6	0.0	0.4	2.6	2.0	1.6	0.5	0.0	0.7	22.4
13'	13.0	0.3	22.9	0.3	0.5	0.0	0.0	1.2	1.1	0.5	0.6	0.0	0.4	16.6
13'2"	13.2	0.6	21.0	0.5	0.5	0.0	0.2	3.0	2.4	0.8	0.8	0.0	1.0	14.9
A13.5a	13.5	0.39	15.22	1.52	1.89	0.00	1.20	1.86	1.07	1.28	1.13	1.17	1.29	12.48
A13.5sd	13.5	0.09	0.86	0.87	0.30	0.00	1.04	0.42	0.31	0.24	0.05	0.31	0.07	0.91
A15a	15.0	0.00	22.70	0.81	4.45	0.00	4.49	3.97	1.95	0.90	0.00	2.08	0.00	24.14
A15sd	15.0	0.00	3.11	1.40	2.07	0.00	3.89	0.57	0.85	1.55	0.00	1.77	0.00	2.97

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Initial Soil Analyses using PLFA – Raw Data (Concluded)															
Sample	Depth (ft)	monounsaturates								brmono		mid-chain branched saturate			poly
		16:1w7t	16:1w5c	cy17:0	18:1w9c	18:1w7c	18:1w7t	18:1w6c	cy19:0	i17:1w7c	br19:1	10me16:0	br17:0	10me18:0	18:2w6c
A0a	0.0	0.48	2.38	3.08	7.89	12.82	0.00	1.15	14.67	2.03	0.90	8.95	2.83	1.98	2.98
A0sd	0.0	0.07	0.36	0.04	1.12	0.46	0.00	0.06	3.70	0.35	0.08	0.99	0.32	0.33	0.27
A2.5a	2.5	0.00	2.62	6.39	12.41	6.08	0.00	0.00	5.21	0.00	0.00	3.26	0.00	2.82	10.23
A2.5sd	2.5	0.00	2.27	1.77	5.37	1.86	0.00	0.00	2.67	0.00	0.00	2.84	0.00	0.42	4.55
A5a	5.0	0.00	1.99	7.13	6.00	15.79	0.00	0.00	15.33	1.78	0.83	3.06	2.57	0.99	2.51
A5sd	5.0	0.00	0.12	0.49	0.62	0.84	0.00	0.00	0.61	0.05	0.08	0.28	0.42	0.09	0.56
52"	5.2	0.6	0.0	6.0	10.2	39.2	3.4	0.0	16.2	0.1	0.7	0.0	0.3	0.0	0.0
54"	5.3	0.5	0.0	6.5	8.0	38.5	3.6	0.0	23.3	0.0	1.3	0.0	0.0	0.0	0.0
56"	5.5	0.3	0.0	7.1	7.2	32.1	3.4	0.0	25.7	0.3	1.8	0.0	0.0	0.0	0.0
58"	5.7	0.2	0.0	6.8	7.1	32.6	3.0	0.0	29.9	0.0	1.5	0.0	0.0	0.0	0.0
510"	5.8	0.0	0.0	7.4	15.1	20.2	1.8	0.0	25.6	0.4	1.0	0.5	2.3	0.0	0.0
6'	6.0	0.0	0.0	8.7	8.9	22.6	1.0	0.0	30.2	0.0	0.5	0.0	0.0	0.4	0.0
62"	6.2	0.0	0.4	10.4	7.0	23.2	0.9	0.0	36.4	0.0	0.6	0.0	0.0	2.1	0.0
64"	6.3	0.6	0.0	11.9	6.8	20.0	0.0	0.0	40.0	0.0	0.0	0.0	0.0	1.1	0.0
66"	6.5	0.0	2.8	6.6	9.1	13.2	1.2	1.5	16.2	0.6	1.4	6.5	5.4	0.0	1.7
A7.5a	7.5	0.92	0.13	6.04	0.65	38.41	2.62	0.00	16.03	0.32	1.28	0.00	0.00	0.00	0.45
A7.5sd	7.5	0.08	0.23	0.48	0.08	8.36	0.49	0.00	3.42	0.12	0.33	0.00	0.00	0.00	0.61
78"	7.7	0.7	0.0	5.8	6.0	43.6	2.7	0.0	13.5	0.0	0.8	0.0	0.0	0.0	0.0
710"	7.8	0.4	0.0	5.0	7.0	53.8	3.1	0.0	15.8	0.0	0.6	0.0	0.0	0.0	0.0
8'	8.0	0.9	0.0	5.9	7.7	40.1	3.8	0.0	15.0	0.8	1.5	0.0	0.0	0.0	0.0
82"	8.2	0.5	0.0	5.7	4.9	44.8	4.4	0.0	14.8	0.4	0.8	0.0	0.0	0.0	0.0
A8.5a	8.5	0.66	0.00	6.29	1.14	44.17	5.91	0.00	17.14	0.42	0.79	0.19	0.00	0.00	0.00
A8.5sd	8.5	0.08	0.00	0.05	0.15	2.40	0.21	0.00	0.69	0.37	0.09	0.32	0.00	0.00	0.00
88"	8.7	0.5	0.0	5.6	4.0	44.4	8.0	0.0	15.9	0.4	0.2	0.0	0.0	0.0	0.0
810"	8.8	0.5	0.0	5.1	4.7	46.2	9.7	0.0	15.1	0.0	0.0	0.0	0.0	0.0	0.0
9'	9.0	0.5	0.0	6.1	4.8	47.2	11.8	0.0	12.0	0.0	0.0	0.0	0.0	0.0	0.0
102"	10.2	0.5	0.6	10.8	6.0	21.9	1.0	0.0	15.6	0.4	0.8	1.3	1.0	0.0	0.0
A10.5a	10.5	0.73	1.42	4.88	10.06	13.89	0.46	0.89	10.40	1.46	0.89	4.89	1.65	1.72	9.47
A10.5sd	10.5	0.11	1.23	0.19	1.50	0.47	0.08	0.05	0.69	0.16	0.05	0.21	0.04	0.12	3.59
A11.5a	11.5	0.85	0.28	8.74	1.24	35.94	5.61	0.00	13.03	0.56	0.21	0.54	0.00	0.00	0.88
A11.5sd	11.5	0.17	0.24	0.16	0.11	3.20	0.31	0.00	1.84	0.22	0.09	0.02	0.00	0.00	0.03
12'	12.0	1.4	0.2	8.0	2.1	32.8	5.9	0.0	17.9	0.0	0.5	0.0	0.1	0.0	0.2
122"	12.2	1.6	0.4	8.9	0.9	27.7	3.0	0.0	21.3	0.0	0.3	0.0	0.0	0.0	0.2
124"	12.3	1.2	0.0	11.3	1.3	26.7	2.1	0.0	16.9	0.1	0.1	0.0	0.0	0.0	0.0
126"	12.5	1.0	0.3	10.5	0.8	26.2	2.8	0.0	21.3	0.0	0.4	0.0	0.0	0.0	0.0
128"	12.7	1.1	0.3	10.6	2.0	23.0	2.5	0.0	8.4	0.1	0.2	0.0	0.0	0.0	0.3
1210"	12.8	1.6	0.5	10.0	1.8	20.8	2.1	0.0	7.2	0.0	0.0	0.0	0.0	0.0	0.0
13'	13.0	1.4	0.0	10.0	3.1	29.0	2.6	0.0	9.3	0.0	0.0	0.0	0.0	0.0	0.0
132"	13.2	1.1	0.0	9.8	3.1	28.7	3.2	0.0	7.9	0.0	0.0	0.0	0.3	0.0	0.0
A13.5a	13.5	1.22	0.00	11.22	1.15	27.96	3.53	0.00	12.36	0.31	1.00	0.0	0.58	0.00	0.16
A13.5sd	13.5	0.05	0.00	0.07	0.06	2.86	0.56	0.00	0.63	0.27	0.20	0.0	0.51	0.00	0.28
A15a	15.0	3.02	0.00	11.66	4.68	9.72	0.00	0.00	2.86	0.00	0.00	0.82	0.00	0.00	1.82
A15sd	15.0	0.25	0.00	3.05	1.43	1.55	0.00	0.00	0.50	0.00	0.00	0.95	0.00	0.00	2.22

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Raw Data – Mineralization

¹⁴ C-phenanthrene (un-saturated)																	
Days		2	6	9	13	15	19	22	26	29	33	36	40	43	47		
Top of the Smear Zone																	
sterile control	avg.	0.03	0.05	0.06	0.06	0.07	0.07	0.06	0.09	0.10	0.10	0.11	0.11	0.12	0.12		
	s.d.	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
control	avg.	0.17	0.49	0.64	0.75	0.82	0.90	0.94	1.04	1.09	1.18	1.24	1.33	1.37	1.44		
	s.d.	0.03	0.07	0.08	0.07	0.05	0.06	0.03	0.10	0.06	0.10	0.07	0.11	0.06	0.06		
H ₂ O ₂ (1.4 mmol)	avg.	0.03	0.05	0.06	0.07	0.08	0.09	0.10	0.12	0.13	0.14	0.15	0.16	0.16	0.19		
	s.d.	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01		
H ₂ O ₂ + nutrients	avg.	0.03	0.04	0.04	0.05	0.05	0.05	0.06	0.07	0.07	0.07	0.08	0.08	0.09	0.09		
	s.d.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
nutrients (N:P:K; 7:7:7)	avg.	0.09	0.11	0.11	0.12	0.12	0.13	0.14	0.15	0.15	0.15	0.16	0.16	0.17	0.17		
	s.d.	0.09	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Bottom of the Smear Zone																	
sterile control	avg.	0.02	0.04	0.05	0.06	0.06	0.07	0.08	0.06	0.09	0.09	0.10	0.11	0.11	0.12		
	s.d.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
control	avg.	0.21	0.30	0.33	0.34	0.35	0.37	0.38	0.39	0.40	0.40	0.41	0.41	0.42	0.42		
	s.d.	0.07	0.05	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
H ₂ O ₂ (1.4 mmol)	avg.	0.06	0.11	0.13	0.14	0.15	0.16	0.16	0.17	0.18	0.18	0.19	0.20	0.20	0.20		
	s.d.	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
H ₂ O ₂ + nutrients	avg.	0.06	0.06	0.08	0.09	0.09	0.10	0.11	0.11	0.12	0.12	0.13	0.14	0.14	0.15		
	s.d.	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
nutrients (N:P:K; 7:7:7)	avg.	0.04	0.06	0.06	0.07	0.07	0.08	0.08	0.09	0.10	0.10	0.10	0.11	0.11	0.12		
	s.d.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		

¹⁴ C-phenanthrene (saturated)																	
Days		0	4	8	12	15	19	22	26	29	33	36	40	43	47		
Top of the Smear Zone																	
sterile control	avg.	0.00	0.01	0.01	0.02	0.03	0.04	0.04	0.05	0.05	0.06	0.07	0.08	0.10	0.11		
	s.d.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.03		
control	avg.	0.00	0.67	1.67	2.78	3.61	4.63	5.29	5.94	6.42	6.96	7.29	7.76	8.06	8.43		
	s.d.	0.00	0.17	0.33	0.54	0.73	0.98	1.20	1.47	1.65	1.83	1.96	2.19	2.29	2.39		
H ₂ O ₂ (1.4 mmol)	avg.	0.00	0.03	0.04	0.05	0.07	0.09	0.10	0.11	0.12	0.13	0.14	0.14	0.15	0.16		
	s.d.	0.00	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03		
H ₂ O ₂ + nutrients	avg.	0.00	0.03	0.03	0.04	0.04	0.05	0.06	0.07	0.07	0.08	0.09	0.11	0.12	0.14		
	s.d.	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.01		
nutrients (N:P:K; 7:7:7)	avg.	0.00	0.55	0.96	1.29	1.49	1.67	1.76	1.88	1.93	1.97	1.98	1.99	2.00	2.01		
	s.d.	0.00	0.16	0.30	0.39	0.44	0.50	0.52	0.56	0.58	0.60	0.61	0.61	0.61	0.61		
Bottom of the Smear Zone																	
sterile control	avg.	0.00	0.01	0.01	0.02	0.03	0.04	0.05	0.05	0.06	0.07	0.08	0.09	0.09	0.10		
	s.d.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
control	avg.	0.00	0.03	0.06	0.09	0.11	0.14	0.16	0.18	0.19	0.20	0.21	0.23	0.24	0.25		
	s.d.	0.00	0.00	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00		
H ₂ O ₂ (1.4 mmol)	avg.	0.00	0.02	0.02	0.03	0.04	0.05	0.06	0.06	0.07	0.08	0.09	0.10	0.11	0.12		
	s.d.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
H ₂ O ₂ + nutrients	avg.	0.00	0.02	0.02	0.03	0.04	0.05	0.07	0.08	0.09	0.09	0.10	0.10	0.11	0.11		
	s.d.	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00		
nutrients (N:P:K; 7:7:7)	avg.	0.00	0.04	0.06	0.08	0.10	0.12	0.13	0.15	0.17	0.19	0.20	0.22	0.23	0.23		
	s.d.	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.00		

¹⁴ C-acetate mineralization (saturated)					¹⁴ C-acetate mineralization (un-saturated)				
hours	Top ¹ (avg)	Top(sd)	Bottom ² (avg)	Bottom(sd)	hours	Top ¹ (avg)	Top(sd)	Bottom ² (avg)	Bottom(sd)
2	1.42	0.18	0.05	0.01	0	0	0	0	0
4	4.53	0.18	0.17	0.01	4	2.57	0.92	0.93	0.08
7	10.43	0.18	0.46	0.01	8	4.61	0.49	1.98	0.34
10	13.65	0.18	0.66	0.01	12	6.67	0.43	2.99	0.28
15	15.83	0.18	0.84	0.01	24	8.29	0.67	4.56	0.63
20	16.66	0.18	0.89	0.01	32	9.49	0.38	5.23	0.34
23	17.79	0.18	0.92	0.01	48	11.41	1.19	6.19	0.19
48	19.24	0.18	0.99	0.01	56	12.09	0.27	6.86	0.24
60	20.91	0.18	1.14	0.01	68	13.4	0.56	7.71	0.21
72	22.34	0.18	1.3	0.01	80	14.04	0.34	8.34	0.3
84	23.85	0.18	1.63	0.01	92	14.63	0.24	8.88	0.29
96	24.78	0.18	1.9	0.01	116	15.78	0.22	9.39	0.13
108	25.22	0.18	2.27	0.01	140	16.87	0.22	10.08	0.27
120	25.6	0.18	2.5	0.01	164	17.67	0.09	10.36	0.07
132	26.3	0.18	2.89	0.01	188	18.73	0.36	10.67	0.03
144	27.9	0.18	3.66	0.01					
168	29.25	0.18	4.45	0.01					
¹ top of the smear zone									
² bottom of the smear zone									

Appendix B

Phase II Natural Attenuation

Data

Fort Drum Area 1595, Natural Attenuation

Location	Date Elapsed Time (days)	12 Aug 0	20 Aug 8	3 Sep 22	18 Sep 37	2 Oct 51	14 Oct 63
Column	H ₂ O added (mL)	525	525	525	525	525	525
	TPH (µg/mL)	1.165	1.165	1.165	1.165	1.165	1.165
	TPH added (µg)	612	612	612	612	612	612
	TPH in air (ng/sccm)						
	Flow rate (sccm/min)						
	Start						
	End						
N1-0	Duration (days)						
	TPH Volatilized (µg)						
	H ₂ O withdrawn (mL)	214	214	214	214	214	214
	TPH (µg/mL)	1.686	0.790	0.339	1.053	1.040	0.910
	TPH withdrawn (µg)	361	169	73	225	223	195
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	3826	0	0	0	0	1055
N1-10	Total rTPH (µg)	4,172,793	0	0	0	0	1,150,904
	H ₂ O withdrawn (mL)	214	214	214	214	214	214
	TPH (µg/mL)	1.78	1.55	0.62	1.50	1.07	1.18
	TPH withdrawn (µg)	382	331	132	322	230	253
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	87	326	0	1608	889	1219
	Total rTPH (µg)	228,386	1,208,421	0	5,963,101	3,298,177	3,191,278
N1-23	H ₂ O withdrawn (mL)	86	86	86	86	86	86
	TPH (µg/mL)	2.17	2.14	0.66	2.40	1.95	1.71
	TPH withdrawn (µg)	187	184	57	206	168	147
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	3895	4524	8019	4574	4066	4992
	Total rTPH (µg)	10,195,681	11,842,545	20,989,958	11,972,681	10,643,275	13,067,511
	Total rTPH (µg)	10,195,681	11,842,545	20,989,958	11,972,681	10,643,275	13,067,511
N1-34	Soil (g)	2286	2286	2286	2286	2286	2286
	rTPH (µg/g)	5468	4204	312	2139	310	959
	Total rTPH (µg)	12,498,680	9,608,777	714,171	4,889,863	708,182	2,193,171
	Soil (g)	2504	2504	2504	2504	2504	2504
	rTPH (µg/g)	9210	17285	0	9711	10369	10879
	Total rTPH (µg)	23,061,712	43,281,391	0	24,315,723	25,964,838	27,240,332
	Total rTPH (µg)	23,061,712	43,281,391	0	24,315,723	25,964,838	27,240,332
N1-58	Soil (g)	2295	2295	3281	3281	3281	2295
	rTPH (µg/g)	10026	7472	9	8847	4925	8335
	Total rTPH (µg)	23,006,807	17,146,362	28,120	29,023,469	16,156,762	19,125,976
	Soil (g)	986	986	0	0	0	986
	rTPH (µg/g)	8617	8234	0	0	0	6987
	Total rTPH (µg)	8,495,539	8,118,164	0	0	0	6,888,126
	Total rTPH (µg)	8,495,539	8,118,164	0	0	0	6,888,126
N2-0	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	10539	0	0	0	0	7184
	Total rTPH (µg)	11,494,034	0	0	0	0	7,834,587
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	4285	180	1377	993	378	2154
	Total rTPH (µg)	11,215,359	668,748	5,106,051	3,683,090	1,400,862	5,637,520
	Total rTPH (µg)	11,215,359	668,748	5,106,051	3,683,090	1,400,862	5,637,520
N2-23	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	42	0	0	0	0	0
	Total rTPH (µg)	109,402	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
N2-34	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	37	101	140	0	0	0
	Total rTPH (µg)	96,828	265,136	365,341	0	0	0
	Total rTPH (µg)	96,828	265,136	365,341	0	0	0
N2-46	Soil (g)	2129	2129	2949	2949	2949	2129
	rTPH (µg/g)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	820	820	0	0	0	820
	rTPH (µg/g)	5	0	0	0	0	0
	Total rTPH (µg)	4,375	0	0	0	0	0
	Total rTPH (µg)	4,375	0	0	0	0	0
N2-58	Soil (g)	820	820	0	0	0	820
	rTPH (µg/g)	5	0	0	0	0	0
	Total rTPH (µg)	4,375	0	0	0	0	0
	Soil (g)	820	820	0	0	0	820
	rTPH (µg/g)	5	0	0	0	0	0
	Total rTPH (µg)	4,375	0	0	0	0	0
	Total rTPH (µg)	4,375	0	0	0	0	0
rTPH (µg) on soil		104,579,594	92,139,544	27,203,641	79,847,927	58,172,097	86,329,405

		Area 1595 Natural Attenuation					
LOCATION	Date	12 Aug	20 Aug	3 Sep	18 Sep	2 Oct	14 Oct
	Time (weeks)	0	1	3	5	7	9
	2-Top	5	0	NS	NS	NS	0
	2-58	0	0	0	0	0	0
	2-46	37	101	140	0	0	0
	2-34	0	0	0	0	0	0
	2-23	42	0	0	0	0	0
	2-10	4285	180	1377	993	378	2154
	2-0	10539	NS	NS	NS	NS	7184
	1-TOP	8617	8234	NS	NS	NS	6987
	1-58	10026	7472	9	8847	4925	8335
	1-46	9210	17285	0	9711	10369	10879
	1-34	5468	4204	312	2139	310	959
	1-23	3895	4524	8019	4574	4066	4992
	1-10	87	326	0	1608	889	1219
	1-0	3826	NS	NS	NS	NS	1055

rTPH on soil in
mg/kg

NS = no sample

Column-Port	Estimated soil volume attributed to sample (cm ³)					
2-TOP	503	503	0	0	0	503
2-58	1305	1305	1808	1808	1808	1305
2-46	1605	1605	1605	1605	1605	1605
2-34	1605	1605	1605	1605	1605	1605
2-23	1605	1605	1605	1605	1605	1605
2-10	1605	2273	2273	2273	2273	1605
2-0	669	0	0	0	0	669
1-TOP	604	604	0	0	0	604
1-58	1407	1407	2011	2011	2011	1407
1-46	1535	1535	1535	1535	1535	1535
1-34	1402	1402	1402	1402	1402	1402
1-23	1605	1605	1605	1605	1605	1605
1-10	1605	2273	2273	2273	2273	1605
1-0	669	0	0	0	0	669
	17723	17723	17723	17723	17723	17723

$$\gamma_d (\text{kN/m}^3) = 16$$

$$\gamma_d (\text{g/cm}^3) = 1.63$$

Column I.D. (in.) = 3.25

Column I.D. (cm) = 8.26

X-section (cm²) = 53.5

Contaminated Soil

Estimated mass of soil = 28,905 g

Estimated mass of contaminated soil = 20,721 g

Indicates that the detected level is below the reporting limit but above the 99% confidence detection limit.

		Area 1595 Natural Attenuation					
LOCATION	Date Time (weeks)	12 Aug 0	20 Aug 1	3 Sep 3	18 Sep 5	2 Oct 7	14 Oct 9
	2-Top						
	2-58	1.6E+08					1.5E+08
	2-46	3.6E+06					2.2E+06
	2-34	1.3E+06					2.4E+06
	2-23	1.6E+08					1.5E+08
	2-10	1.7E+08					1.4E+08
	2-0						
	1-TOP						
	1-58	5.9E+08					6.6E+08
	1-46	1.9E+08					1.6E+08
	1-34	5.7E+08					2.8E+08
	1-23	9.6E+07					1.7E+08
	1-10	5.4E+07					9.6E+07
	1-0						
biomass in soil (cells/g soil)		2.0E+09					1.8E+09

LOCATION	2-Top						
	2-58	6525					5908
	2-46	146					87
	2-34	50					95
	2-23	6494					5951
	2-10	6996					5758
	2-0						
	1-TOP						
	1-58	23654					26348
	1-46	7517					6428
	1-34	22722					11312
	1-23	3830					6810
	1-10	2166					3847
	1-0						
PLFA in soil (pmole/g)							

~ 25,000 cells/
pmol PLFA

Appendix C

Phase II Bioventing Data

Fort Drum Area 1595, Bioventing

Location	Date	12 Aug	20 Aug	3 Sep	18 Sep	2 Oct	14 Oct
	Elapsed Time (days)	0	8	22	37	51	63
Column	H ₂ O added (mL)	525	525	525	525	525	525
	TPH (µg/mL)	1.165	1.165	1.165	1.165	1.165	1.165
	TPH added (µg)	612	612	612	612	612	612
	TPH in air (ng/secm)		1.21	1.21	1.21	1.21	1.21
	Flow rate (scm/min)		4	4	4	1	1
	Start		8/13/97 19:00	8/21/97 17:00	9/4/97 23:00	9/19/97 19:10	10/3/97 12:45
	End		8/20/97 17:00	9/3/97 22:00	9/18/97 8:00	10/2/97 10:00	10/13/97 15:53
	Duration (days)		6.92	13.21	13.38	12.62	10.13
V1-0	TPH Volatilized (µg)		48	92	93	22	18
	H ₂ O withdrawn (mL)	214	214	214	214	214	214
	TPH (µg/mL)	0.502	0.675	0.278	0.915	0.885	0.975
	TPH withdrawn (µg)	107	144	60	196	189	209
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	0	0	0	0	0	0
V1-10	Total rTPH (µg)	0	0	0	0	0	0
	H ₂ O withdrawn (mL)	214	214	214	214	214	214
	TPH (µg/mL)	0.86	0.92	0.54	1.25	1.08	1.10
	TPH withdrawn (µg)	184	197	115	268	231	235
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	9	101	51	39	112	16
V1-23	Total rTPH (µg)	24,021	376,088	190,870	144,498	413,472	42,021
	H ₂ O withdrawn (mL)	86	86	86	86	86	86
	TPH (µg/mL)	7.72	2.16	0.49	1.84	1.99	1.32
	TPH withdrawn (µg)	664	186	42	159	171	113
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	4839	2832	6689	3930	2976	1946
V1-34	Total rTPH (µg)	12,666,148	7,411,480	17,508,983	10,286,128	7,790,702	5,094,236
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	4981	2876	6377	2035	1012	1821
	Total rTPH (µg)	13,036,227	7,528,389	16,691,737	5,325,608	2,648,302	4,766,013
	Soil (g)	2504	2504	2504	2504	2504	2504
	rTPH (µg/g)	8012	15468	9504	6957	10889	9754
V1-46	Total rTPH (µg)	20,063,348	38,733,217	23,798,702	17,420,493	27,265,109	24,423,732
	Soil (g)	2296	2296	3284	3284	3284	2296
	rTPH (µg/g)	6217	8134	6680	7062	5169	4330
	Total rTPH (µg)	14,277,322	18,677,892	21,938,669	23,190,228	16,976,043	9,942,751
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	2806	2526	0	0	0	3764
V1-TOP	Total rTPH (µg)	2,771,529	2,494,995	0	0	0	3,717,546
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	2749	0	0	0	0	3119
	Total rTPH (µg)	2,998,427	0	0	0	0	3,401,280
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	1272	526	474	500	472	573
V2-0	Total rTPH (µg)	3,330,565	1,949,261	1,756,016	1,854,138	1,751,539	1,500,125
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	0	0	0	0	0	3898
	Total rTPH (µg)	0	0	0	0	0	10,203,234
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	0	0	0	0	0	0
V2-34	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	0	0	0	0	0	0
V2-46	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	2296	2296	3284	3284	3284	2296
	rTPH (µg/g)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	0	0	0	0	0	0
V2-58	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	0	0	0	0	0	0
V2-TOP	Total rTPH (µg)	0	0	0	0	0	0
	rTPH (µg) on soil	69,167,587	77,171,322	81,884,976	58,221,092	56,845,166	63,090,940
	TPH degraded (µg) based on respiration data		616,150	701,641	279,896	105,263	67,097

		Area 1595 Bioventing					
LOCATION	Date	12 Aug	20 Aug	3 Sep	18 Sep	2 Oct	14 Oct
	Time (weeks)	0	1	3	5	7	9
	2-Top	0	0	NS	NS	NS	0
	2-58	0	0	0	0	0	0
	2-46	0	0	0	0	0	0
	2-34	0	0	0	0	0	0
	2-23	0	0	0	0	0	3898
	2-10	1272	526	474	500	472	573
	2-0	2749	NS	NS	NS	NS	3119
	1-TOP	2806	2526	NS	NS	NS	3764
	1-58	6217	8134	6680	7062	5169	4330
	1-46	8012	15468	9504	6957	10889	9754
	1-34	4981	2876	6377	2035	1012	1821
	1-23	4839	2832	6689	3930	2976	1946
	1-10	9	101	51	39	112	16
	1-0	0	NS	NS	NS	NS	0

rTPH on soil in
mg/kg

NS = no sample

Column-Port	Estimated soil volume attributed to sample (cm ³)					
2-TOP	606	606	0	0	0	606
2-58	1408	1408	2014	2014	2014	1408
2-46	1605	1605	1605	1605	1605	1605
2-34	1605	1605	1605	1605	1605	1605
2-23	1605	1605	1605	1605	1605	1605
2-10	1605	2273	2273	2273	2273	1605
2-0	669	0	0	0	0	669
1-TOP	606	606	0	0	0	606
1-58	1408	1408	2014	2014	2014	1408
1-46	1535	1535	1535	1535	1535	1535
1-34	1605	1605	1605	1605	1605	1605
1-23	1605	1605	1605	1605	1605	1605
1-10	1605	2273	2273	2273	2273	1605
1-0	669	0	0	0	0	669
	18133	18133	18133	18133	18133	18133

$$\gamma_d (\text{kN/m}^3) = 16$$

$$\gamma_d (\text{g/cm}^3) = 1.63$$

Column I.D. (in.) = 3.25
Column I.D. (cm) = 8.26
X-section (cm²) = 53.5

Contaminated Soil

Estimated mass of soil = 29,575 g
Estimated mass of contaminated soil = 17,348 g

mark also both yellow and red
described above

1555 Bioventing				Tank		Plotted Time of Sample (days)	Elapsed Time (days)	Flow Rate @ Inlet (scfm)						
Sample Start	Sample End	Sample	O ₂	CO ₂	O ₂				O ₂	CO ₂	O ₂	ΔO ₂	ΔCO ₂	CO ₂
			Sample (% by Vol.)	Sample (% by Vol.)	Sample (% by Vol.)				Sample (% by Vol.)	Sample (% by Vol.)	Consumed	(% by Vol.)	(% by Vol.)	Produced
8/13/97 19:00	8/14/97 21:00	8/14/97 21:00	20.20%	0.05%	0.05%	0.5	1.1	4	16.91%	2.33%	0.0190	4.07%	2.30%	0.0125
8/14/97 21:00	8/15/97 19:30	8/15/97 19:30	20.17%	0.05%	0.05%	1.6	2.0	4	17.97%	2.12%	0.0381	3.02%	2.09%	0.0124
8/15/97 19:30	8/18/97 0:15	8/18/97 0:15	20.98%	0.03%	0.03%	3.1	4.2	4			0.0616			0.0152
8/18/97 0:15	8/20/97 17:00	8/20/97 17:00	20.99%	0.03%	0.03%	5.6	6.9	4	18.58%	1.71%	0.0908	2.37%	1.67%	0.0189
8/21/97 17:00	8/25/97 21:15	8/25/97 21:15	20.95%	0.04%	0.04%	9.0	12.1	4	18.49%	1.76%	0.1118	2.46%	1.72%	0.0138
8/25/97 21:15	8/28/97 20:00	8/28/97 20:00	20.95%	0.04%	0.04%	13.6	15.0	4	19.59%	1.27%	0.1272	1.36%	1.23%	0.0136
8/28/97 20:00	9/1/97 22:00	9/1/97 22:00	20.95%	0.04%	0.04%	17.1	19.1	4	20.12%	0.80%	0.1292	0.83%	0.76%	0.0083
9/1/97 22:00	9/2/97 19:00	9/2/97 19:00	20.95%	0.04%	0.04%	19.6	20.0	4			0.0026			0.0023
9/2/97 19:00	9/3/97 22:00	9/3/97 22:00	20.95%	0.04%	0.04%	21.1	21.1	4	20.00%	0.74%	0.1318	0.94%	0.71%	0.0071
9/4/97 23:00	9/8/97 16:30	9/8/97 16:30	20.94%	0.02%	0.02%	23.0	25.9	4	20.06%	0.70%	0.1447	0.88%	0.68%	0.0020
9/8/97 16:30	9/9/97 18:15	9/9/97 18:15	20.95%	0.03%	0.03%	26.4	27.0	4	20.24%	0.65%	0.1464	0.71%	0.62%	0.0014
9/9/97 18:15	9/10/97 14:00	9/10/97 14:00	20.95%	0.03%	0.03%	27.4	27.8	4	20.35%	0.55%	0.1497	0.62%	0.52%	0.0027
9/10/97 14:00	9/12/97 11:45	9/12/97 11:45	21.14%	0.04%	0.04%	28.7	29.7	4	20.55%	0.51%	0.1514	0.59%	0.51%	0.0014
9/12/97 11:45	9/13/97 12:20	9/13/97 12:20	20.94%	0.03%	0.03%	30.2	30.7	4	20.39%	0.52%	0.1544	0.55%	0.49%	0.0026
9/13/97 12:20	9/15/97 12:00	9/15/97 12:00	20.92%	0.03%	0.03%	31.7	32.7	4	20.23%	0.55%	0.1566	0.55%	0.52%	0.0015
9/15/97 12:00	9/16/97 14:00	9/16/97 14:00	20.94%	0.03%	0.03%	33.3	33.8	4	20.28%	0.56%	0.1598	0.66%	0.53%	0.0015
9/16/97 14:00	9/17/97 14:30	9/17/97 14:30	20.95%	0.04%	0.04%	34.3	34.8	4	20.33%	0.53%	0.1598	0.62%	0.51%	0.0010
9/17/97 14:30	9/18/97 8:00	9/18/97 8:00	20.92%	0.04%	0.04%	35.2	35.5	4	19.37%	0.95%	0.1653	1.55%	0.91%	0.0030
9/19/97 19:10	9/24/97 14:00	9/24/97 14:00	20.95%	0.04%	0.04%	37.9	41.8	1	19.22%	1.15%	0.1676	1.58%	1.12%	0.1162
9/24/97 14:00	9/26/97 14:00	9/26/97 14:00	20.80%	0.03%	0.03%	42.8	43.8	1	19.62%	1.05%	0.1686	1.34%	1.02%	0.1170
9/26/97 14:00	9/27/97 15:15	9/27/97 15:15	20.96%	0.04%	0.04%	44.3	44.8	1	20.40%	0.61%	0.1698	0.59%	0.56%	0.0011
9/27/97 15:15	9/30/97 14:00	9/30/97 14:00	20.99%	0.03%	0.03%	46.3	47.8	1			0.1702			0.0004
9/30/97 14:00	10/1/97 14:00	10/1/97 14:00	21.00%	0.04%	0.04%	48.3	48.8	1	20.83%	0.56%	0.1703	0.27%	0.52%	0.0003
10/1/97 14:00	10/2/97 10:00	10/2/97 10:00	21.10%	0.05%	0.05%	49.2	49.6	1	19.73%	0.91%	0.1728	1.22%	0.88%	0.0017
10/3/97 12:45	10/6/97 10:00	10/6/97 10:00	20.95%	0.03%	0.03%	51.1	53.6	1	20.09%	0.75%	0.1737	0.86%	0.72%	0.0007
10/6/97 10:00	10/7/97 20:00	10/7/97 20:00	20.95%	0.04%	0.04%	54.3	55.0	1	20.11%	0.70%	0.1742	0.84%	0.67%	0.0004
10/7/97 20:00	10/8/97 16:00	10/8/97 16:00	20.95%	0.04%	0.04%	55.5	55.9	1	20.14%	0.67%	0.1748	0.82%	0.64%	0.0004
10/8/97 16:00	10/9/97 14:30	10/9/97 14:30	20.96%	0.03%	0.03%	56.3	56.8	1	20.13%	0.66%	0.1752	0.82%	0.63%	0.0003
10/9/97 14:30	10/10/97 9:40	10/10/97 9:40	20.95%	0.03%	0.03%	57.2	57.6	1	20.20%	0.64%	0.1765	0.76%	0.61%	0.0010
10/10/97 9:40	10/12/97 20:00	10/12/97 20:00	20.96%	0.03%	0.03%	58.8	60.0	1	20.18%	0.63%	0.1770	0.79%	0.60%	0.0003
10/12/97 20:00	10/13/97 15:53	10/13/97 15:53	20.97%	0.03%	0.03%	60.5	60.9	1						0.1236

Linear estimation of cumulative O ₂ consumption from day 42 to 61			
O ₂ consumption rate (moles/day) = 0.000573	0.142 = y intercept		
standard error of slope = 0.000017	0.001 = standard error of y intercept		
coefficient of determination = 0.991	0.000366 = standard error of y estimates		
F statistic = 1181	11 = degrees of freedom		
regression sum of squares = 0.000158	0.0000015 = residual sum of squares		

Linear estimation of cumulative CO ₂ production from day 42 to 61			
CO ₂ consumption rate (moles/day) = 0.000445	0.0966 = y intercept		
standard error of slope = 0.000009	0.0005 = standard error of y intercept		
coefficient of determination = 0.995	0.000207 = standard error of y estimates		
F statistic = 2224	11 = degrees of freedom		
regression sum of squares = 0.00010	0.0000005 = residual sum of squares		

All sample measurements made @ 10°C
and 1 atmosphere.

LOCATION	Date Time (weeks)	Area 1595 Bioventing					
		12 Aug 0	20 Aug 1	3 Sep 3	18 Sep 5	2 Oct 7	14 Oct 9
	2-Top						
	2-58	4.8E+07					3.7E+07
	2-46	2.0E+07					1.5E+07
	2-34	9.2E+07					3.2E+07
	2-23	2.0E+08					1.4E+08
	2-10	1.5E+08					1.0E+08
	2-0						
	1-TOP						
	1-58	2.2E+08					2.7E+08
	1-46	2.6E+08					3.0E+08
	1-34	2.4E+08					2.9E+08
	1-23	1.4E+08					1.2E+08
	1-10	2.6E+06					1.3E+07
	1-0						

biomass in soil
(cells/g soil)

1.4E+09

1.3E+09

	2-Top						
	2-58	1906					1482
	2-46	805					613
	2-34	3675					1293
	2-23	7851					5764
	2-10	6029					4119
	2-0						
	1-TOP						
	1-58	8636					10863
	1-46	10573					12010
	1-34	9644					11501
	1-23	5512					4698
	1-10	104					510
	1-0						

PLFA in soil
(pmole/g)

~ 25,000 cells/
pmol PLFA

Appendix D

Phase II Biosparging Data

Fort Drum Area 1595, Biosparging

Location	Date Elapsed Time (days)	12 Aug 0	20 Aug 8	3 Sep 22	18 Sep 37	2 Oct 51	14 Oct 63
Column	H ₂ O added (mL)	525	525	525	525	525	525
	TPH (µg/mL)	1.165	1.165	1.165	1.165	1.165	1.165
	TPH added (µg)	612	612	612	612	612	612
	TPH in air (mg/sec)		15.3	15.3	15.3	15.3	15.3
	Flow rate (scfm/min)		4	4	4	1	1
	Start		8/13/97 19:00	8/21/97 17:00	9/4/97 23:00	9/19/97 19:10	10/3/97 12:45
	End		8/20/97 17:00	9/3/97 22:00	9/18/97 8:00	10/2/97 10:00	10/13/97 15:53
	Duration (days)		6.92	13.21	13.38	12.62	10.13
S1-0	TPH Volatilized (µg)		608	1,161	1,176	277	223
	H ₂ O withdrawn (mL)	214	214	214	214	214	214
	TPH (µg/mL)	0.633	0.655	0.843	0.951	0.961	0.844
	TPH withdrawn (µg)	135	140	180	203	206	181
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	0	0	0	0	0	0
S1-10	Total rTPH (µg)	0	0	0	0	0	0
	H ₂ O withdrawn (mL)	214	214	214	214	214	214
	TPH (µg/mL)	1.55	2.29	1.16	2.01	1.93	1.10
	TPH withdrawn (µg)	333	490	248	431	413	236
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	5990	3917	3397	4833	2990	1650
S1-23	Total rTPH (µg)	15,679,315	14,523,995	12,596,657	17,919,885	11,085,245	4,319,158
	H ₂ O withdrawn (mL)	86	86	86	86	86	86
	TPH (µg/mL)	7.23	1.09	0.489	0.284	0.405	0.107
	TPH withdrawn (µg)	622	94	42	24	35	9
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	3199	2565	2349	3165	2088	2674
S1-34	Total rTPH (µg)	8,374,209	6,714,365	6,149,011	8,284,764	5,464,758	6,999,760
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	3401	1560	1915	319	198	81
	Total rTPH (µg)	8,902,422	4,082,733	5,013,627	833,864	517,529	211,098
	Soil (g)	2172	2172	2172	2172	2172	2172
	rTPH (µg/g)	135	2	1504	295	3804	1562
S1-46	Total rTPH (µg)	292,869	5,107	3,266,573	641,784	8,263,322	3,393,713
	Soil (g)	1963	1963	2617	2617	2617	1963
	rTPH (µg/g)	13107	5470	9528	5659	5241	4574
	Total rTPH (µg)	25,730,717	10,738,665	24,938,206	14,812,035	13,718,921	8,979,104
	Soil (g)	654	654	0	0	0	654
	rTPH (µg/g)	5777	4598	0	0	0	5456
S1-TOP	Total rTPH (µg)	3,780,187	3,008,694	0	0	0	3,570,440
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	5303	0	0	0	0	7700
	Total rTPH (µg)	5,783,744	0	0	0	0	8,397,466
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	2363	646	1814	2302	1929	1304
S2-0	Total rTPH (µg)	6,186,016	2,393,690	6,724,961	8,535,848	7,153,763	3,413,520
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	172	0	0	0	0	0
	Total rTPH (µg)	449,875	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	96	0	0	0	0	0
S2-10	Total rTPH (µg)	251,560	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
	Soil (g)	2296	2296	3284	3284	3284	2296
	rTPH (µg/g)	195	63	0	0	0	0
S2-23	Total rTPH (µg)	447,793	144,871	0	0	0	0
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	0	152	0	0	0	0
	Total rTPH (µg)	0	149,959	0	0	0	0
	Soil (g)	2296	2296	3284	3284	3284	2296
	rTPH (µg/g)	195	63	0	0	0	0
S2-34	Total rTPH (µg)	447,793	144,871	0	0	0	0
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	0	152	0	0	0	0
	Total rTPH (µg)	0	149,959	0	0	0	0
	Soil (g)	2296	2296	3284	3284	3284	2296
	rTPH (µg/g)	195	63	0	0	0	0
S2-46	Total rTPH (µg)	447,793	144,871	0	0	0	0
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	0	152	0	0	0	0
	Total rTPH (µg)	0	149,959	0	0	0	0
	Soil (g)	2296	2296	3284	3284	3284	2296
	rTPH (µg/g)	195	63	0	0	0	0
S2-58	Total rTPH (µg)	447,793	144,871	0	0	0	0
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	0	152	0	0	0	0
	Total rTPH (µg)	0	149,959	0	0	0	0
	Soil (g)	2296	2296	3284	3284	3284	2296
	rTPH (µg/g)	195	63	0	0	0	0
S2-TOP	Total rTPH (µg)	447,793	144,871	0	0	0	0
	Soil (g)	988	988	0	0	0	988
	rTPH (µg/g)	0	152	0	0	0	0
	Total rTPH (µg)	0	149,959	0	0	0	0
	Soil (g)	2296	2296	3284	3284	3284	2296
	rTPH (µg/g)	195	63	0	0	0	0
rTPH (µg) on soil		75,878,708	41,762,079	58,689,035	51,028,182	46,203,538	39,284,258
TPH degraded (µg) based on respiration data			386,033	646,327	333,507	138,370	93,410

		Area 1595 Biosparging					
LOCATION	Date	12 Aug	20 Aug	3 Sep	18 Sep	2 Oct	14 Oct
	Time (weeks)	0	1	3	5	7	9
	2-Top	0	152	NS	NS	NS	0
	2-58	195	63	0	0	0	0
	2-46	0	0	0	0	0	0
	2-34	96	0	0	0	0	0
	2-23	172	0	0	0	0	0
	2-10	2363	646	1814	2302	1929	1304
	2-0	5303	NS	NS	NS	NS	7700
	1-TOP	5777	4598	NS	NS	NS	5456
	1-58	13107	5470	9528	5659	5241	4574
	1-46	135	2	1504	295	3804	1562
	1-34	3401	1560	1915	319	198	81
	1-23	3199	2565	2349	3165	2088	2674
	1-10	5990	3917	3397	4833	2990	1650
	1-0	0	NS	NS	NS	NS	0

rTPH on soil in
mg/kg

NS = no sample

Column-Port	Estimated soil volume attributed to sample (cm ³)					
2-TOP	606	606	0	0	0	606
2-58	1408	1408	2014	2014	2014	1408
2-46	1605	1605	1605	1605	1605	1605
2-34	1605	1605	1605	1605	1605	1605
2-23	1605	1605	1605	1605	1605	1605
2-10	1605	2273	2273	2273	2273	1605
2-0	669	0	0	0	0	669
1-TOP	401	401	0	0	0	401
1-58	1204	1204	1605	1605	1605	1204
1-46	1332	1332	1332	1332	1332	1332
1-34	1605	1605	1605	1605	1605	1605
1-23	1605	1605	1605	1605	1605	1605
1-10	1605	2273	2273	2273	2273	1605
1-0	669	0	0	0	0	669
	17521	17521	17521	17521	17521	17521

$$\gamma_d (\text{kN/m}^3) = 16$$

$$\gamma_d (\text{g/cm}^3) = 1.63$$

Column I.D. (in.) = 3.25

Column I.D. (cm) = 8.26

X-section (cm²) = 53.5

Contaminated Soil

Estimated mass of soil = 28,577 g

Estimated mass of contaminated soil = 16,350 g

Indicates that the detected level is below the reporting limit but above the 99% confidence detection limit.

1595 Biosparging									
Sample		Elapsed Time (days)	Plotted Time of Sample (days)	Flow Rate @ Inlet (scfm)	Tank		O ₂ consumption		
Start	End				O ₂ Sample (% by Vol.)	CO ₂ Sample (% by Vol.)	O ₂ Sample (% by Vol.)	ΔO ₂ (% by Vol.)	O ₂ Consumed (mol)
Sample Start	Sample End	Elapsed Time (days)	Plotted Time of Sample (days)	Flow Rate @ Inlet (scfm)	O ₂ Sample (% by Vol.)	CO ₂ Sample (% by Vol.)	O ₂ Sample (% by Vol.)	ΔO ₂ (% by Vol.)	O ₂ Consumed (mol)
8/13/97 19:00	8/14/97 21:00	1.1	0.5	4	20.20%	0.05%	18.28%	1.92%	0.0062
8/14/97 21:00	8/15/97 19:30	2.0	1.6	4	20.17%	0.05%	18.16%	2.01%	0.0056
8/15/97 19:30	8/18/97 0:15	4.2	3.1	4	20.98%	0.03%	19.14%	1.84%	0.0120
8/18/97 0:15	8/20/97 17:00	6.9	5.6	4	20.99%	0.03%	19.11%	1.88%	0.0148
8/21/97 17:00	8/25/97 21:15	12.1	9.0	4	20.95%	0.04%	19.38%	1.57%	0.0132
8/25/97 21:15	8/28/97 20:00	15.0	13.6	4	20.95%	0.04%	19.31%	1.64%	0.0192
8/28/97 20:00	9/1/97 22:00	19.1	17.1	4	20.95%	0.04%	19.41%	1.54%	0.0039
9/1/97 22:00	9/2/97 19:00	20.0	19.6	4	20.95%	0.04%	19.41%	1.54%	0.0039
9/2/97 19:00	9/3/97 22:00	21.1	20.6	4	20.95%	0.04%	19.51%	1.44%	0.0050
9/3/97 22:00	9/6/97 16:30	25.9	23.0	4	20.94%	0.02%	19.77%	1.17%	0.0035
9/6/97 16:30	9/9/97 18:15	27.0	26.4	4	20.95%	0.03%	20.11%	0.84%	0.0019
9/9/97 18:15	9/10/97 14:00	27.8	27.4	4	20.95%	0.03%	20.30%	0.67%	0.0036
9/10/97 14:00	9/12/97 11:45	29.7	28.7	4	21.14%	0.04%	20.46%	0.68%	0.0020
9/12/97 11:45	9/13/97 12:20	30.7	30.2	4	20.94%	0.03%	20.63%	0.31%	0.0016
9/13/97 12:20	9/15/97 12:00	32.7	31.7	4	20.94%	0.03%	20.22%	0.70%	0.0022
9/15/97 12:00	9/16/97 14:00	33.8	33.3	4	20.92%	0.03%	20.27%	0.67%	0.0019
9/16/97 14:00	9/17/97 14:30	34.8	34.3	4	20.95%	0.04%	20.32%	0.63%	0.0013
9/17/97 14:30	9/18/97 8:00	35.5	35.2	4	20.92%	0.04%	18.88%	2.04%	0.0074
9/18/97 8:00	9/24/97 14:00	41.8	37.9	1	20.80%	0.03%	19.25%	1.55%	0.0022
9/24/97 14:00	9/26/97 14:00	43.8	42.8	1	20.96%	0.04%	19.72%	1.24%	0.0009
9/26/97 14:00	9/27/97 15:15	44.8	44.3	1	20.99%	0.03%	20.03%	0.99%	0.0020
9/27/97 15:15	9/30/97 14:00	47.8	46.3	1	21.00%	0.04%	20.03%	0.97%	0.0007
9/30/97 14:00	10/1/97 14:00	48.8	48.3	1	21.10%	0.05%	20.07%	1.03%	0.0006
10/1/97 14:00	10/2/97 10:00	49.6	49.2	1	20.95%	0.03%	19.63%	1.32%	0.0029
10/3/97 12:45	10/6/97 10:00	53.6	51.1	1	20.95%	0.04%	19.44%	1.51%	0.0016
10/6/97 10:00	10/7/97 20:00	55.0	54.3	1	20.95%	0.04%	19.77%	1.18%	0.0007
10/7/97 20:00	10/8/97 16:00	55.9	55.5	1	20.95%	0.04%	19.78%	1.18%	0.0008
10/8/97 16:00	10/9/97 14:30	56.8	56.3	1	20.95%	0.03%	19.77%	1.18%	0.0007
10/9/97 14:30	10/10/97 9:40	57.6	57.2	1	20.95%	0.03%	19.85%	1.11%	0.0019
10/10/97 9:40	10/12/97 20:00	60.0	58.8	1	20.95%	0.03%	19.68%	1.29%	0.0008
10/12/97 20:00	10/13/97 15:53	60.9	60.5	1	20.97%	0.03%	19.68%	1.29%	0.0008

Linear estimation of cumulative O ₂ consumption from day 42 to 61									
O ₂ consumption rate (moles/day) = 0.000803	0.1107 = y intercept								
standard error of slope = 0.000011	0.0006 = standard error of y intercept								
coefficient of determination = 0.998	0.000239 = standard error of y estimates								
F statistic = 5424	11 = degrees of freedom								
regression sum of squares = 0.000311	0.0000006 = residual sum of squares								

Linear estimation of cumulative CO ₂ production from day 42 to 61									
CO ₂ consumption rate (moles/day) = 0.000535	0.0706 = y intercept								
standard error of slope = 0.000013	0.0007 = standard error of y intercept								
coefficient of determination = 0.993	0.000287 = standard error of y estimates								
F statistic = 1664	11 = degrees of freedom								
regression sum of squares = 0.0001	0.0000009 = residual sum of squares								

All sample measurements made @ 10°C and 1 atmosphere.

		Area 1595 Biosparging					
LOCATION	Date Time (weeks)	12 Aug 0	20 Aug 1	3 Sep 3	18 Sep 5	2 Oct 7	14 Oct 9
	2-Top						
	2-58	2.4E+07					3.4E+06
	2-46	1.5E+08					5.5E+07
	2-34	1.1E+08					4.1E+07
	2-23	4.4E+07					1.3E+07
	2-10	8.1E+07					2.7E+07
	2-0						
	1-TOP						
	1-58	2.9E+08					1.3E+08
	1-46	6.4E+07					4.4E+07
	1-34	9.7E+07					9.3E+07
	1-23	1.0E+08					1.3E+08
	1-10	2.6E+07					8.8E+06
	1-0						
biomass in soil (cells/g soil)		9.9E+08					5.4E+08

LOCATION	2-Top		
	2-58	949	137
	2-46	5841	2204
	2-34	4546	1624
	2-23	1755	510
	2-10	3234	1076
	2-0		
	1-TOP		
	1-58	11776	5084
	1-46	2542	1740
	1-34	3897	3729
	1-23	4015	5280
	1-10	1028	351
	1-0		

PLFA in soil
(pmole/g)

~ 25,000 cells/
pmol PLFA

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14. ABSTRACT The U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, under scope of work agreement with the U.S. Army Engineer District, Baltimore, conducted a biological treatability study to evaluate three alternative remediation strategies and provide information useful for the design and implementation of long-term remediation activities for Area 1595 of Gasoline Alley, Fort Drum, New York. The project was executed between March and October 1997. The objectives of the evaluation were to: (a) determine potential microbial activity of Area 1595 subsurface soils; (b) determine intrinsic TPH degradation potential of Area 1595 subsurface microorganisms; (c) determine parameters which will enhance subsurface microbial growth in Area 1595; (d) optimize parameters using column study simulation of Area 1595 subsurface conditions; and (e) generate data for design and preliminary cost evaluation for the remediation of Area 1595. This document reports the final analysis of treatability evaluations for Area 1595.					
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